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Hydrogenation

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ABSTRACT

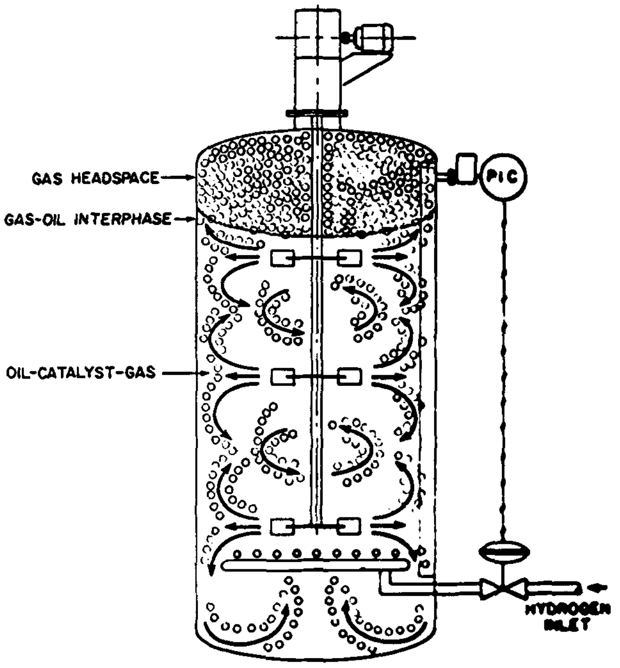
Hydrogenation of vegetable oils as it is practiced today is described as theory and process. Double bonds in the fatty acid portions of the oils are saturated with hydrogen and rearranged to produce many isomers during the process.

Hydrogenation of vegetable oils is a rather recent development that has had a great impact on the agriculture and food industry throughout the world. After discovery by Normann in 1902, the liquid phase hydrogenation was brought to the United States about 1920. It has grown into the large industry of today. Although the basic process has been used for many years and billions of pounds of products have been prepared, the reaction has never been fully understood; it is extremely complicated, occurring only when the liquid vegetable oil, hydrogen gas and solid catalyst are brought together under the correct set of conditions.

Batch hydrogenators are rather simple equipment, consisting of a tank, a pump to get the oil and catalyst in and out, a perforated pipe to put the hydrogen into the tank as small bubbles, and an agitator. A typical hydrogenator is shown in Figure 1. This shows the bubbles of hydrogen rising through the oil-catalyst mixture and collecting in the headspace while the agitator circulates the gas bubbles so the gas will dissolve in the oil, go to the catalyst and meet the unsaturated vegetable oil. Thus, the 3 reactants are brought together.

To understand this, an individual catalyst particle and an individual bubble of hydrogen are shown in Figure 2. The gas A is being dissolved in the oil both from the headspace and the bubble, migrating to the solid catalyst particle where it reacts with the double bond B to form the product C, releasing some heat to the surrounding oil. However, it really is not so simple, as shown in Figure 3. To reach the surrounding oil, the hydrogen must migrate first through the stagnant layer surrounding the bubble then into the oil so that the concentration is lowered. When hydrogen reaches the catalyst particle, a layer must also be penetrated; again, this resistance lowers the total concentration of hydrogen. Also, the unsaturated oil must penetrate the barrier to reach the catalyst so that the concentration of unsaturated oil is also decreased. Only with very vigorous agitation will these resistances be overcome and then only the kinetics, temperature and pressure will control the speed of hydrogenation. Most commercial hydrogenators are "underagitated," meaning the rate of reaction is controlled by the rate of migration of the hydrogen and double bonds to the catalyst surface. Although temperature and pressure affect the kinetics, the main effect of these reaction parameters is on the rate of migration of the hydrogen.

When the hydrogen and double bond meet at the catalyst surface, a reaction occurs. Unfortunately, we do not know what actually happens on the surface or in the catalyst pores because our knowledge is limited about the catalyst surface or pores. In fact, we know more about the



TYPICAL GAS BUBBLE FLOW PATTERN FOR HIGH MIXER HORSEPOWER

FIG. 1. Batch hydrogenator.

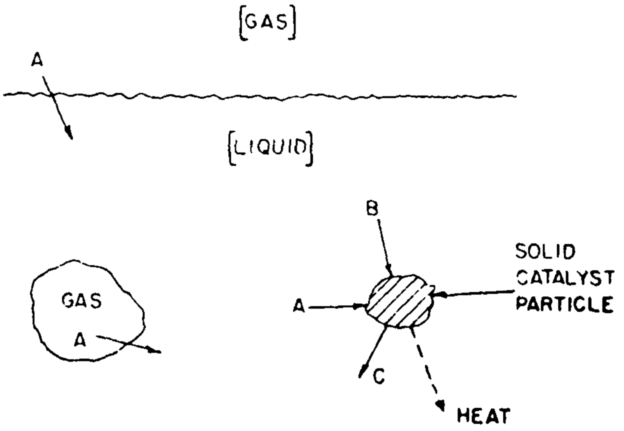


FIG. 2. Individual catalyst particle and gas bubble.

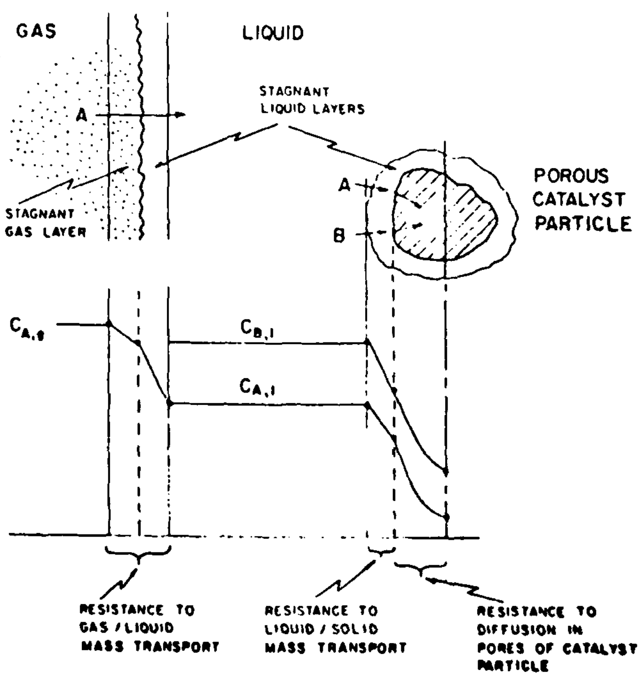


FIG. 3. Change in concentration of hydrogen during migration.

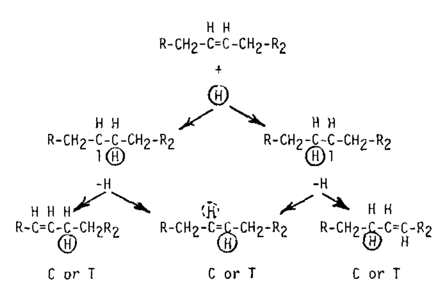


FIG. 4. Hydrogenation and isomerization of oleate.

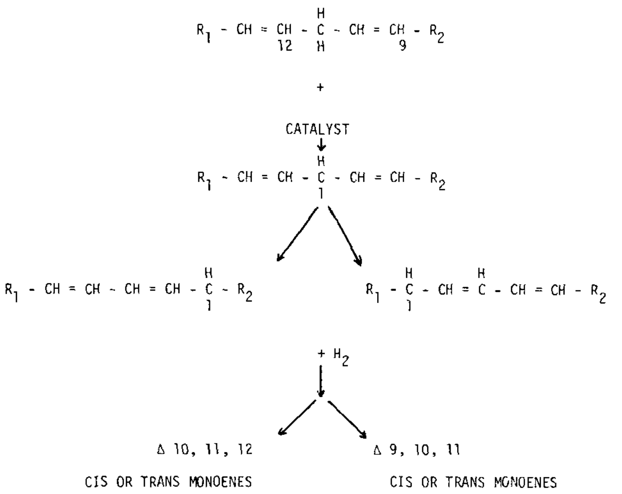


FIG. 5. Hydrogenation and isomerization of linoleate.

surface of the planet Jupiter than we know about the catalyst surface. However, from analysis of the products formed in the reaction of unsaturated oils with catalyst and hydrogen, we can make an educated guess at what happens on the surface. When methyl oleate is partially hydrogenated, analysis of the products shows that the double bond is not only saturated, but the remaining bonds also are isomerized, moved along the chain (positional isomerism) and are converted from *cis* to *trans* form (geometrical isomerism). As shown in Figure 4, if the hydrogen exists on the catalyst surface as hydrogen atoms, the double bond opens and a hydrogen atom can add at either end of the unsaturation. If the catalyst surface is covered with hydrogen, another atom will be added and the bond becomes saturated. However, if the catalyst surface is not covered with hydrogen, an atom of hydrogen may be removed from either side of the partially saturated bond, thus forming a new double bond in the original position or moved one carbon away. Thus, the double bond will migrate either way and the new double bonds may be *cis* or *trans*. Of course, the double bonds in the new positions may also go through this half-hydrogenation-dehydrogenation sequence and the new double bonds are moved even further from the original position. The new bond may be *cis* or *trans*.

Also, as shown in Figure 5, if the linoleic system of the methylene-interrupted double bond system is hydrogenated, the hydrogens on the methylene group between the 2 double bonds are very labile; if a hydrogen is removed, a bond shifts to form a conjugated system which hydrogenates very rapidly to form a monoene. This is shown by the analysis of the monoene produced from partial hydrogenation of linoleic acid. Most of the remaining double bonds are in the 10- or 11-position, not the original 9-, 12-positions.

The theory of atomic hydrogenation has evolved, which seems to explain these observations. If the hydrogenation is done at high pressure, low temperature, high agitation and low levels of catalyst, the catalyst surface is covered with hydrogen and there is limited geometrical and positional isomerism. Also, the "selectivity" of the reaction is low, as is the *trans* unsaturation. However, high temperature, low agitation, low pressure and high catalyst load results in incomplete coverage of the catalyst surface with hydrogen so that both positional and geometrical isomerization is high, and the selectivity and *trans* unsaturation content are high.

To illustrate selectivity, the hydrogenation curve for soybean oil is shown in Figure 6. As the hydrogenation proceeds, the linolenic acid goes to linoleic, then to oleic then to saturation. However, all the unsaturated bonds are hydrogenating at the same time, but at different rates. If we assume the reaction is first order, i.e., the speed depends on the concentration of the unsaturated acids, then the reaction rate constants are K_1, K_2 and K_3 and can be estimated by a computer from the time-compositional data.

The circles in Figure 6 are the observed data and the line is the composition calculated from the first order reaction rate constants. Selectivity is defined as the rate of one reaction compared to the rate of another reaction. Thus, if we divide K_1 by K_2, the linolenic selectivity of 2.3 is obtained. The linolenic acid is hydrogenated 2.3 times faster than the linoleic acid.

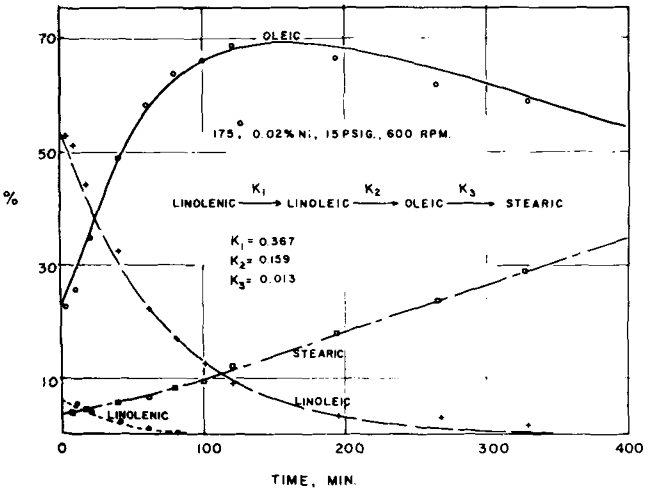


FIG. 6. Hydrogenation of soybean oil.

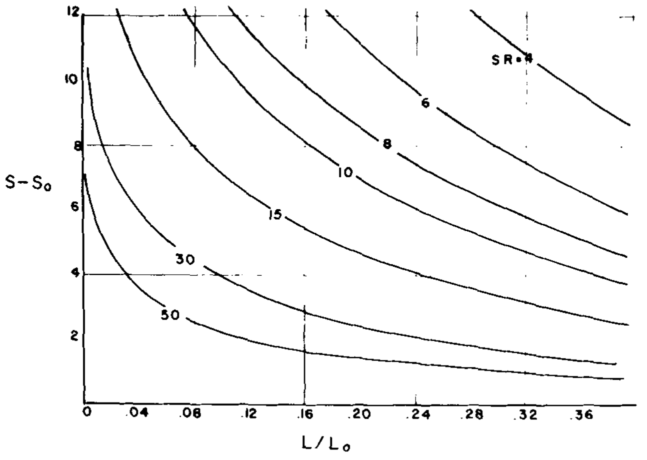


FIG. 7. Estimation of selectivity (LS).

The linolenic selectivity of the usual nickel catalyst does not change with changes in process conditions. As the 8-carbon triene system in linolenic can be considered as two 5-carbon diene systems, the rate of hydrogenation of the linolenic system could be twice that of linoleic. Because the comparative rate is slightly over 2,2.3-2.4, probably the presence of the third double bond has some effect.

If K_2 is divided by K_3, the linoleic selectivity (LS) of 12 is obtained. The LS of 12 means the linoleic is being hydrogenated 12 times faster than the oleic. As stated earlier, the linoleic selectivity, SR or LS, depends on temperature, pressure, catalyst concentration, agitation and type of catalyst.

Figure 7 shows a graph to estimate the LS value from the products of hydrogenation of soybean oil. As shown, the gain in stearic acid and the ratio of beginning and ending linoleic will give the selectivity ratio, LS.

Different catalysts will give different selectivity values. Only recently have catalyst manufacturers learned how to produce catalysts with high selectivity values in response to the edible fat and oil processors' demand for this type of catalyst. These catalysts enable the processor to reduce the linoleic without producing too much stearic, thus producing a product with good oxidative stability and a low melting point.

The relationship of the selectivity of a particular catalyst used under various temperature, pressure and catalyst levels is shown in Figure 8. With a good, selective catalyst, the reaction parameters of temperature, pressure and agitation may be selected to produce almost any hydrogenation product.

An increase in the amount of *trans* unsaturation also increases the melting point of the hydrogenated fat product. Because all hydrogenations produce some *trans* unsaturation, the reaction parameters must be controlled to produce the desired amount of *trans*. Figure 9 shows the effect of temperature and pressure on the *trans* unsaturation of soybean oil hydrogenated to 80 IV. The selectivity characteristics of a catalyst are unrelated to the catalyst ability to form *trans*, because catalysts may have very low or very high selectivities, but it seems all common nickel catalysts produce the same amount of *trans* at the same conditions. However, catalysts may be treated with other

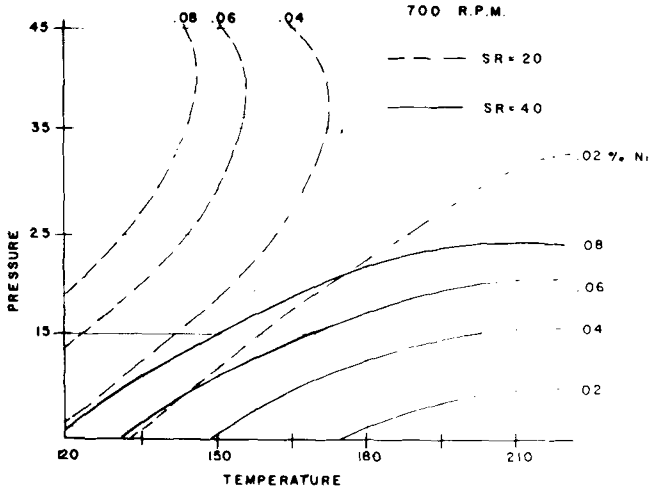


FIG. 8. Temperature, pressure and catalyst concentration effect on selectivity.

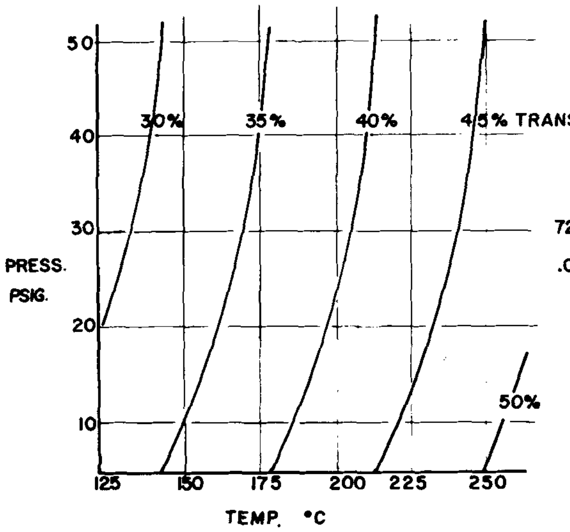


FIG. 9. Effect of temperature and pressure on *trans* unsaturation of soybean oil at 80 IV.

materials, such as sulfur, which increases the amount of *trans* unsaturation.

Although the mechanism of the reaction using sulfur-treated catalysts has not been defined, it appears a sulfur-nickel complex causes the isomerization and any unreacted nickel in the catalyst causes the hydrogenation. Thus, these catalysts are a mixture of 2 catalysts that assist separate reactions.

Looking to the future, one of the great needs in our industry is for a hydrogenation catalyst that will result in hydrogenations of, e.g., dienes and trienes, to monoenes, without formation of any *trans* unsaturation. This would make possible the use of highly unsaturated oils for the production of good flavor, stable salad oils without further processing to remove high-melting glycerides. Thus, in spite of the enormous amount of reach in hydrogenation, there still remain some fundamental problems that need more research.

Practical Aspects of Hydrogenation and Soybean Salad Oil Manufacture

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ABSTRACT

Most edible oils are hydrogenated in batch-type slurry converters similar in basic design to those employed when the process was first commercialized in 1911. One major company uses a proprietary continuous slurry process. Other novel batch and continuous slurry systems are available but have not enjoyed significant commercial success. Fixed bed hydrogenation has not been seriously investigated but offers intriguing possibilities. Energy economy is assuming ever greater importance in the design of hardening systems. The accelerated growth of hydrogenation since the 1940s parallels the rapid increase in soybean oil use. In part, it reflects the flavor instability of soybean oil caused by its linolenic ester. When this triunsaturate is lowered by hydrogenation to ca. 3%, a high-quality soybean salad oil can be produced. Standard hydrogenation and separation techniques work well. New separation equipment and processes are entering the marketplace.

Fats have always been a significant part of the human diet, contributing the fuel necessary for energy expenditure. When our ancestors were migrant hunters, their intake of fat was indirect, being consumed as meat and seeds. The rise of agriculture, along with the domestication of animals, resulted in the invention of processes to obtain fats and oils as separate entities. These included the rendering of fat from meat, the pressing of oil from grain or fruit, and the concentration of fats from milk. Obvious examples are lard, olive oil and butter. These processes served the human race well for thousands of years, changing eating habits from opportunity, i.e., "what did we kill or find today," to planned cooking.

The greatly expanding urban population during the Industrial Revolution readied civilization for the invention of a new process that would both improve existing natural fat and oil products and also pave the way for large-quantity production of high-quality, alternate products. That new process was hydrogenation.

Sabatier (1) is usually credited with discovering hydrogenation. His 1897 bench work was quickly picked up by William Normann, who obtained a British patent on liquid-phase hydrogenation in 1903 (2). Procter & Gamble acquired U.S. rights to the Normann patent in 1909 and began marketing Crisco, a vegetable shortening containing hydrogenated fat, in 1911. Note that the time interval from bench discovery through process patent to commercial use was only 14 years and involved 3 entirely disconnected groups in different countries. It is doubtful that we could move as speedily today. Of course, in 1900, there were no government requirements for feeding tests or Environmental Impact Statements, and that certainly shortened the process.

Fortunately for the fats and oils industry, Procter & Gamble's exclusive rights to the hydrogenation process, as spelled out in the Normann patent, were invalidated by the U.S. courts in a short time and the way was cleared for similar shortenings to be manufactured and marketed by others. What sort of products were these? Principally what we, today, call compounds, consisting of either ca. 15% fully hydrogenated cottonseed oil (stearine) blended with refined cottonseed oil, or ca. 10% fully hydrogenated lard added to unhydrogenated lard. Considerable quantities of compounded vegetable shortenings and fortified lard are still consumed in the world today, particularly in less technologically advanced countries.

The next quantum leap in edible oil hydrogenation occurred in the 1930s, when U.S. packaged food processors began the mass marketing of 2 products. One was all-hydrogenated vegetable shortening. This increased the hydrogenated portion of the formulation 5-6-fold. The other was oleomargarine as a butter substitute. While oleomargarine had been around for a long time, its generally poor quality, the availability of butter at a relatively low price, and a 10¢/lb federal tax if it was colored, kept it from becoming very popular. Consumer demand, along with the political clout of the rapidly increasing number of soybean farmers, resulted in the tax finally being repealed in 1948. The soybean's time had come; Figure 1 (3) shows how far it has progressed in the United States. We are familiar with the more recent phenomenal increase of soybean production in other countries, particularly Brazil.

The first major use of soybean oil was in margarine