Principles and Catalysts for Hydrogenation of Fats and Oils

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ABSTRACT

Hydrogenation of vegetable oils has been practiced since the discovery by Normann some 75 years ago and is the major chemical process in the fat and oil industry. Hydrogenation changes a liquid oil to a semisolid fat which has more utility and better flavor stability. The reaction is not a simple saturation of double bonds with hydrogen, but is an extremely complex series of reactions that result in a myriad of products. By control of the reaction conditions, pressure, temperature, agitation, and catalyst type and concentration, the desired product may be obtained. The use of new equipment and methods has produced some understanding of the hydrogenation reactions. This knowledge has allowed the production of better, more consistent products designed for use by the consumer.

The hydrogenation of vegetable oils was discovered by Normann some seventy-five years ago and since then has developed into the major chemical process in fat and oil industry. The whole oil seed industry resulted from the ability to hydrogenate the by-product oil produced by extraction of the seed and thus lowered the cost of the protein part of the seed that is used for animal feed. The whole growth of the soybean industry paralleled the growth of hydrogenation of food oils. In 1975 in the U.S., some 7.3 billion lbs. of oil was hydrogenated. If we estimate catalyst usage at .02% Ni, then 1.5 million lbs. of nickel was used. Also, if we guess the average IV drop was 35 (from 125 IV to 90), then 3.6 billion cu. ft. of hydrogen was used. Thus, this is an important industry.
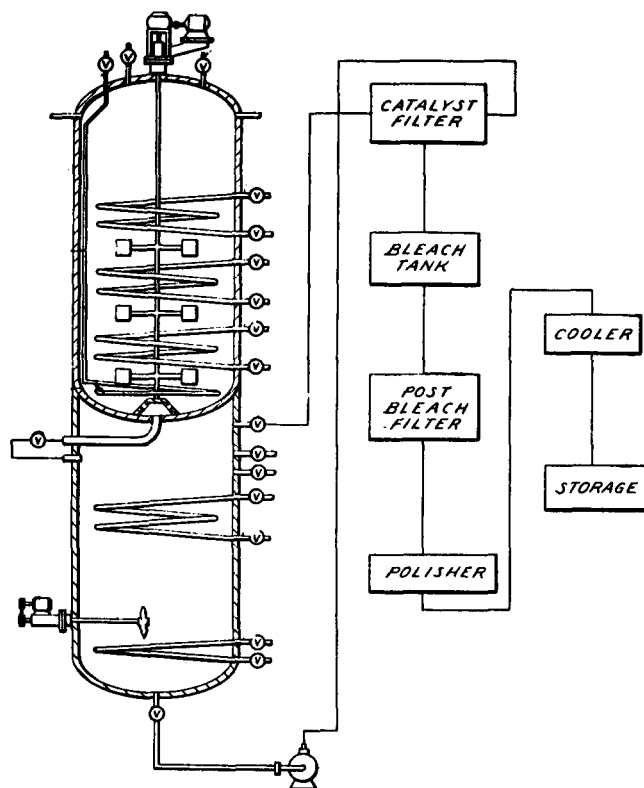

FIG. 1. Batch hydrogenation apparatus.

There are two reasons to hydrogenate oils. First, since the number of double bonds is reduced, the opportunity for oxidation is decreased, and thus the flavor stability is increased. Second, the physical characteristics are changed so the product has more utility. Products such as margarines, shortenings, coating fats, frying fats all result from hydrogenation of oils. Also, a myriad of inedible products are made such as alcohols, amines, amides, etc., by hydrogenation of fats or acids, but this report will be confined to the edible fat industry.

Most undergraduate chemistry textbooks show the hydrogenation of oils as a simple saturation of double bonds in an unsaturated fat with hydrogen using nickel as a catalyst. Actually, this is only one of a set of very complex reactions.

Batch hydrogenation equipment is actually rather simple (Figure 1). Essentially all that is necessary is a vessel that can stand 50-60 psig, an agitator, means for heating and cooling, a hydrogen inlet, piping and pumps to deliver the oil in and out, and a sampling pipe to follow the course of the reaction. The equipment provides the means to control three parameters of the reaction: pressure, temperature and rate of agitation.

The pressure of the hydrogen in the reaction is usually measured in the headspace of the reactor and controls the hydrogen inlet valve. Also, the headspace may be vented to get rid of gaseous impurities such as methane, nitrogen, carbon dioxide and carbon monoxide. Also, some hydrogen gas is lost. Venting also causes an increase in the hydrogen flow through the reaction mass which increases the agitation. The agitation is the sum of several effects. The type of agitator blades and their speed are the primary agitation, but the type and number of heating and cooling coils and any baffels, as well as the speed of hydrogen inlet through the perforated sparger ring in the bottom of the reactor, all contribute to the effect called agitation.

Heating of the oil is usually accomplished by Dowtherm or high pressure steam coils. For the usual nickel catalyst, temperatures of 140-225 C. are used for hydrogenation, and the higher temperatures are achieved by starting the reaction at some lower temperature and allowing the exothermic heat of reaction to provide the heat necessary for high temperature operation.

In practice the oil is pumped into the converter, a vacuum pulled on the headspace and heating started. Meanwhile, the catalyst is weighed into the catalyst mix tank, slurried with a small amount of oil, and as soon as the gassing temperature is reached, the catalyst is pumped into the reactor, mixed, and then hydrogen is added to the desired pressure. The reaction will start, and the temperature is increased to the operating temperature and maintained by cooling the reaction mass. The course of the reaction is followed by a change in refractive index.

The oil going to hydrogenation must be refined, bleached, low soap (under 25 ppm), and dry.

The hydrogen must be dry and as high hydrogen content as possible. The newer plants that produce hydrogen from hydrocarbons will produce extremely pure hydrogen, while the older plants produce hydrogen with some methane, carbon dioxide and may contain considerable nitrogen if the starting gas contained much nitrogen. Since liquid hydrogen is available, some plants have been designed to obtain the gas from storage of the liquid. This also furnishes a good source for standby gas if the gas plant is shut down. Liquid hydrogen is very pure.

The catalyst is a critical element for hydrogenation. Nickel is used almost exclusively except for some special products. A catalyst must be active, have a long life, selective, and have known isomer formation which is easily removed by filtration and consistent from batch to batch. About 15 years ago a very selective active consistent catalyst was offered so that today the catalysts available are vastly improved over those some 15 years ago. The old type catalysts, and some are still used today, were prepared from nickel formate. The nickel formate was mixed with an oil and heated until the formate decomposed. Metallic nickel was produced and reduced by the hydrogen produced by the formate. Unfortunately, if heated too long, some nickel particles became collodial in size and consequently very difficult to filter out of the hydrogenated oils. The newer type catalysts are dry reduced and may contain another metal as a promoter. Also, the particle size permits rapid filtration with no collodial nickel particles in the oil. Although it may look economical to prepare your own catalyst, it is best to purchase the catalyst since very high quality catalysts are offered by catalyst manufacturers.

The activity of a catalyst determined how much catalyst is needed to hydrogenate a batch of oil in a reasonable time. Activity may be defined as iodine value decrease per unit of time during a hydrogenation under a specific set of conditions. The AOCS has a Recommended Practice Method, No. Ca 17-76, that compares the time to hydrogenate SBO to 80 IV at 350 F., 20 psig using 0.05% test catalyst compared to the time used by a standard catalyst that may be obtained from the AOCS office. Thus, activity of catalysts may be compared and used as part of a purchase specification.

The life of a catalyst determines how long a catalyst will remain active and useful. Of course, the life may be decreased by poisons such as sulfure compounds, fatty acids, phosphatides, etc., in the oil. A good catalyst may be used several times although the percentage may need to be increased slightly for each reuse to compensate for the decrease in activity. However, the selectivity, which will be discussed later, will change on catalyst reuse. Therefore, many fat and oil manufacturers specify new catalysts for manufacture of critical base stocks and accumulate the catalysts for reuse to prepare fully hydrogenated material or hard stock where selectivity is not important.

The selectivity of a catalyst or hydrogenation reaction may be explained by consideration of the sequence of reactions that occur during a hydrogenation. Figure 2 shows the typical hydrogenation curves of an oil high in diene, linoleic. As the hydrogenation proceeds, the diene is reduced to a monoene by hydrogenation of one double bond. At the same time, the monoene is reduced to a saturated or stearic. The reaction sequence of the hydrogenation of linolenic acid, the three double bond acid, is the first double bond is hydrogenated; linoleic and iso-linoleic acids are produced. These are then hydrogenated to oleic or elaidic (trans), which are then hydrogenated to stearic. Of course, there may be several detours. In the three double bond acid, any one of the three double bonds may be hydrogenated, leaving the other two. The product that is formed is dependent on which of the double bonds was hydrogenated. At the same time, some of the double bonds are saturated, some may be shifted to a new position and also twisted to the higher melting trans form. Of course, a natural oil, such as soybean oil or cottonseed oil, already contains the series of unsaturated fatty acids. The hydrogenation of a natural oil thus is complicated by the fact not only is the most unsaturated molecule hydrogenating, but at the same time all the others that are present in the starting material may be hydrogenating. The rates at which these reactions occur is the selectivity of the reaction. The selectivity term has been used in the past by
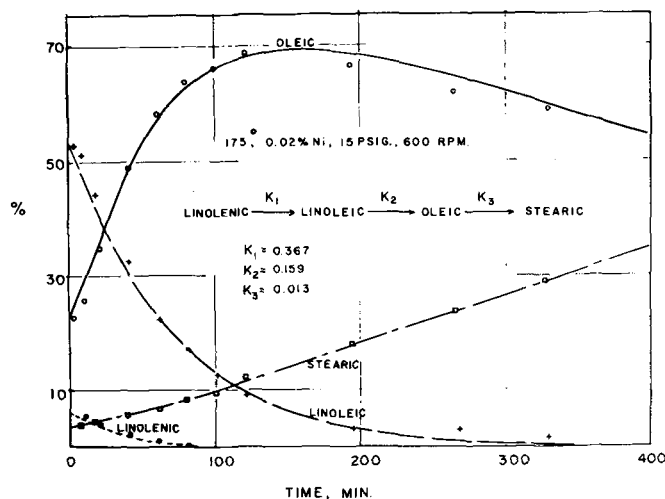

FIG. 2. Hydrogenation of soybean oil.

fat and oil processors in the sense that the hydrogenated product should be as soft as possible at a low iodine value or a minimum melting point, cloud point, congeal point for a given iodine value. Thus, the definition of selectivity in this way would be only a relative term. In the past the hydrogenation reactions have been said to be selective, nonselective, and some word descriptions that were vague were used to describe the selectivity. Thus, what one person may call very selective would not be the same to another worker in the field. However, if selectivity is defined as the ratio of reaction rates, then one can make a much more absolute term. In the March, 1965 Journal, Dr. Albright of Purdue University published a number of graphs that we have found very useful in assigning a selectivity number to a catalyst. Thus, catalysts may be judged by this selectivity number. This selectivity number as defined in Albright's publication is simply the ratio of the hydrogenation of linoleic acid compared to the hydrogenation of oleic acid. As shown in Figure 2, a very simplified reaction sequence, K_1 is a reaction rate of the hydrogenation of linolenic acid to linoleic. K_2, linoleic to oleic and K_3, oleic to stearic acid. The selectivity ratio then is defined as the ratio of K_2 over K_3, for the reaction shown $K_2/K_3 = 0.159/013 = 12.2$. For example, a selectivity ratio of 12 means that the linoleic acid is being hydrogenated at 12 times the rate of the oleic acid. A selectivity ratio of 50 would mean the linoleic acid is hydrogenated 50 times the rate of the oleic acid. To determine the selectivity ratio, one needs to know the analysis of the beginning oil and the hydrogenated product. Of course, by the use of gas liquid chromatography this is quite a simple analysis. By the use of a computer, the pseudo first order reaction rate constants K_1, K_2 and K_3 may be calculated from the starting and ending fatty acid composition and the time of hydrogenation. The rates shown in Figure 2 were calculated, and the values then need to calculate the composition shown by the lines. The points are experimental values.

Since a computer is not always available to calculate the rate constants, the graphs published by Albright may be used. These graphs were prepared by calculation of the fatty acid composition at various selectivity ratios. For example, Figure 3 shows a graph for the calculation of the selectivity ratio of soybean oil hydrogenation. In the original paper, the y axis of the graph was shown as a delta IV, which means the IV drop due to the excess hydrogenation to stearic acid. However, we have found that the delta IV term is actually an increase in the amount of stearic that is formed during the hydrogenation. Thus, the ratio of the starting and final linoleic acid that is present in the final
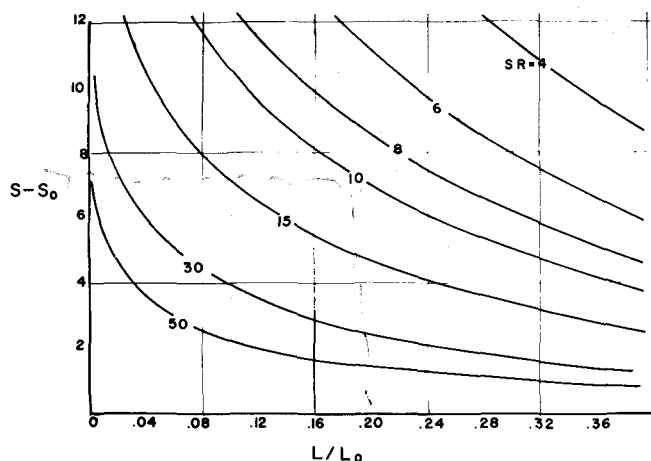
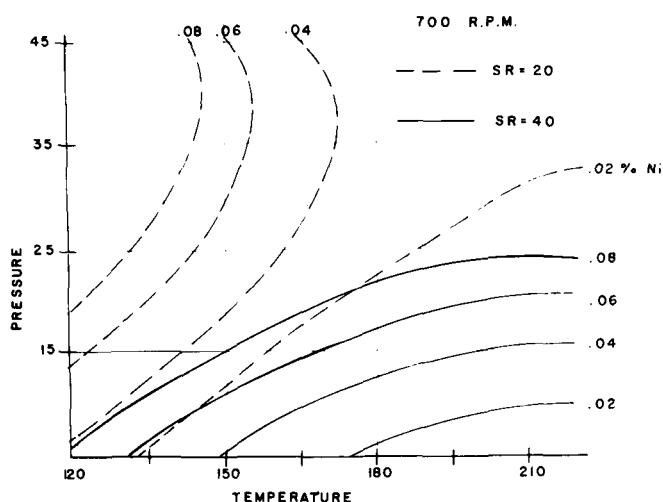FIG. 3. Estimation of SR from the change in fat composition.

FIG. 4. Effects of pressure, temperature and catalyst on SR.

FIG. 5. Effects of pressure, temperature on SR.

FIG. 6. Effects of agitation and catalyst concentration on SR.

product compared to the amount of stearic acid that is formed during the hydrogenation, change in stearic, gives the selectivity ratio. For example, if .2 of the linoleic remained after hydrogenation adn 7% stearic was formed during the reaction, the selectivity ratio would be about 10. This would mean that the linoleic acid was hydrogenated 10 times faster than the oleic acid. As can be seen from the graph, if one has perfect selectivity, in other words the selectivity ratio is infinite, then no stearic acid would be formed, although all of the linoleic acid would be hydrogenated to oleic. These curves were calculated by assuming several things: one, that the reaction rates were first order, and another, that the trans or iso-oleic hydrogenates at the same rate as the oleic. These assumptions are simplifying assumptions and are probably valid, at least for use in this type of study.

Thus, catalysts may be selected on the basis of their selectivity characteristics. We have tested catalysts that show SR or selectivity ratios of from 2 to 70. Since the SR is a measure of the amount of stearic formed as the linoleic is reduced, the catalysts that show the highest selectivities should be used. Thus, more linoleic may be reduced to increase stability before much saturates are formed so the product will not be too hard.

The process conditions also affect the SR value. Figure 4 shows the effect of pressure, temperature and catalyst concentration on the SR value. As shown, the higher temperatures, lower pressures, and higher catalyst concentration show higher SR values. Figure 5 also shows the effect of
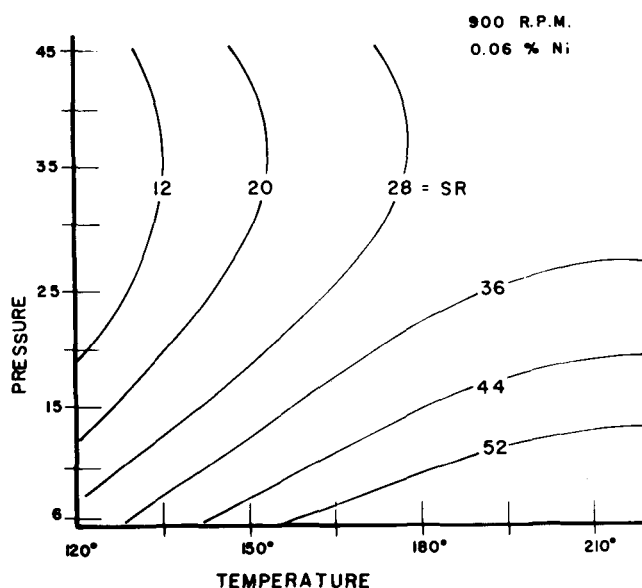
pressure and temperature on the SR value.

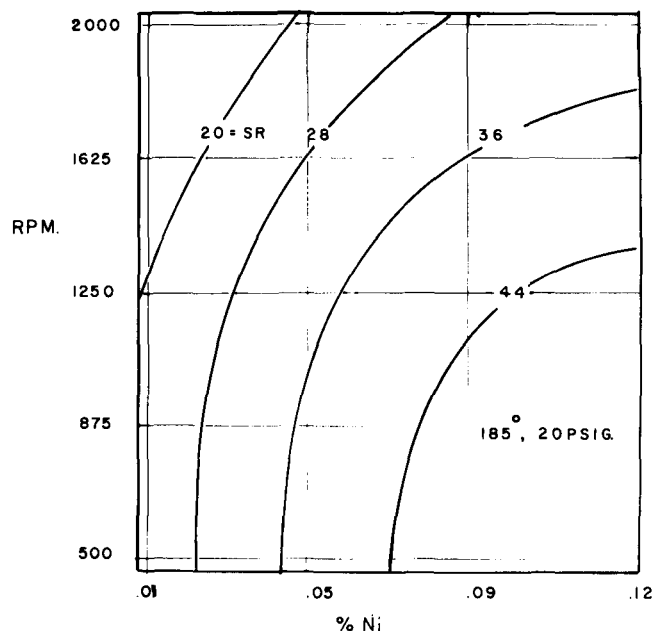Another reaction parameter that affects the selectivity ratio to a great extent is the degree of agitation of the reacting mixture. Agitation during a hydrogenation must accomplish a number of things. It must whip the hydrogen into the reaction mixture so that it can dissolve and, thus, be available. The catalyst must be suspended throughout the oil mixure so that it may come in contact with the hydrogen and with the unsaturated carbon chains. And, also, the agitation must dissipate the heat of the reaction and not allow any over heating or hot spots in the reaction. Figure 6 shows the effects of agitation and catalyst concentration on the SR. As shown, at a catalyst concentration, an increase in the agitation, shown as RPM of the agitator, decreases the SR. Also, at a rate of agitation, an increase in catalyst concentration increases the SR. However, at high catalyst loads, the rate of change of the SR with catalyst is decreasing.

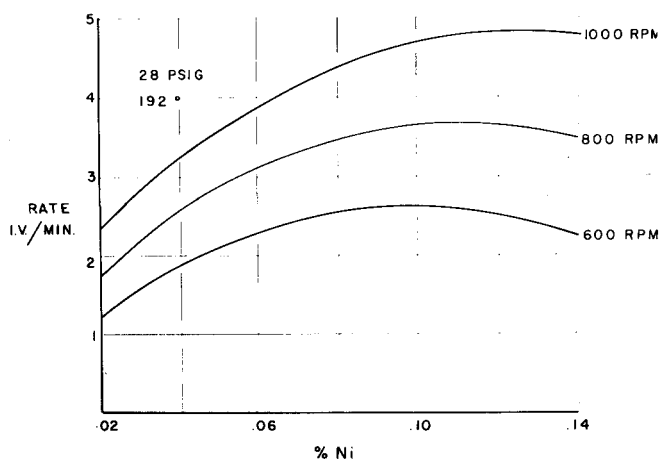Agitation also affects the rate of hydrogenation as

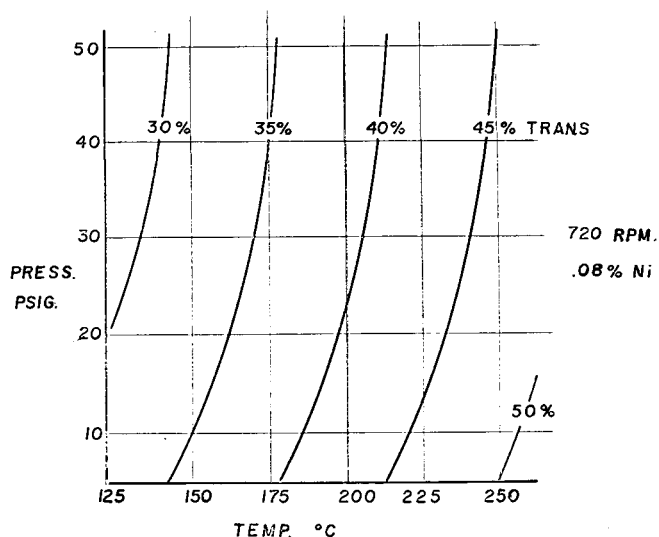FIG. 7. Effects of agitation and catalyst concentration on rate.

FIG. 8. Effects of pressure and temperature on trans unsaturation at 80 I.V. soybean oil.

shown in Figure 7. At an agitation rate, an increase in catalyst increases the rate of hydrogenation, but the change in rate decreases as the catalyst increases. The change in agitation increases the rate of hydrogenation, but the magnitude of the rate is increased at the higher catalyst loads. Thus, the agitation, catalyst load, temperature and pressure must be selected to give the best rate to produce the desired product.

This change in selectivity ratio with agitation furnishes a very useful means for matching laboratory or pilot plant hydrogenations to plant equipment. Most plant equipment is of such size that the agitation rate is considerably less than the rate that is needed to eliminate the resistance to mass transfer. Also, the internal structure of each of the converters affects the agitation. To match small equipment to the plant, the agitation rate of the small equipment is adjusted to obtain the same selectivity ratio using the same oil, catalyst, temperature and pressure as the plant. Usually with two or three trail batches, one may match up the equipment and thus be able to produce the same product in the laboratory or pilot plant as the plant equipment produces.

Therefore, to test catalysts for selectivity, a set of process conditions must be selected and all catalysts tested under these conditions so the results will be comparable.

Another factor to consider in catalyst selection is the isomerization characteristics. During hydrogenations many of the cis bonds are changed to both positional and trans isomers. The amount of trans affects the solids content of the fat at low temperatures, so it must be controlled. Unless a catalyst contains some added material such as sulfure to increase the formation of trans, most nickel catalysts form the same amount of trans under the same conditions although the selectivity may vary widely. The trans is controlled by the process conditions as shown in Figure 8. As the temperature of the reaction is increased, the trans at any IV is increased, but as the pressure is increased, the trans is decreased.

These changes in process conditions and their effects on SR, Trans and the rates of reaction are summarized. If other conditions are held constant and:

The temperature increased; SR increases, trans increases, rate increases.

The pressure increased; SR decreases, trans decreases, rate increases.

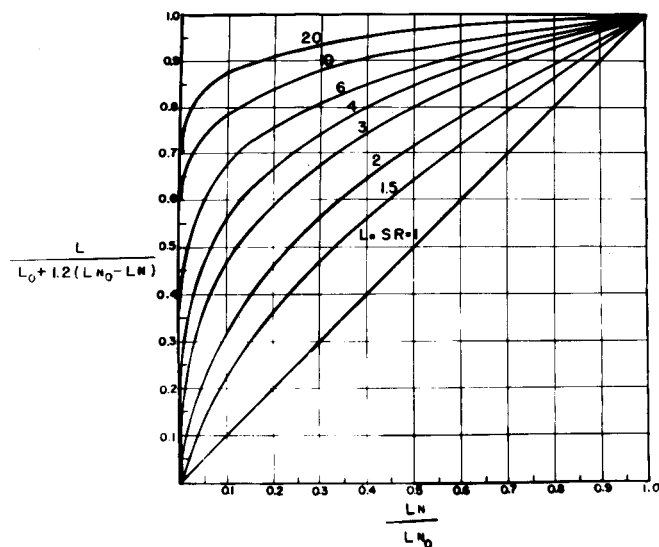The agitation increased; SR decreases, trans decreases, rate increases.

FIG. 9. Estimation of linolenic SR from starting and ending fatty acid composition.

The catalyst increased; SR increases, trans increases, rate increases.

Another type of selectivity that is quite important is the linolenic selectivity, LnSR or the ratio of the rate of hydrogenation of linolenic acid compared to the rate of reaction of linoleic acid. A method to estimate the LnSR is shown in Figure 9. Since the flavor reversion of soybean oil is believed to be due to the linolenic moiety or triene, the hydrogenation of linolenate without hydrogenation of linoleate is quite important. Nickel catalysts show a linolenate selectivity of about 2 and are not changed by process conditions, which indicates the diene and triene are hydrogenated by the same mechanism. However, work at the USDA Lab in Peoria has shown copper chromite catalysts have a linolenic SR of 10 to 15. Thus the linolenate may be reduced to a low amount before much linoleate is reduced. However, these catalyst have found very limited industrial use because of several other problems.