Hydrogenation: Principles and Catalysts[1]

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Abstract

The hydrogenation reaction is the most important chemical reaction in the fat and oil industry. It is also perhaps the least understood.

The most critical factor in the reaction is the catalyst. Several different types of metal catalysts can be used. The reaction conditions as well as other factors determine the type of product produced. However, all the factors can be related to effects on the catalyst.

The "selectivity" concept of catalyst evaluation is not new. However, the term has come to have several different meanings. It is believed the term should be used only for chemical selectivity which can be easily determined. The "selectivity ratio" number is very useful and can be used to judge the performance of a catalyst.

Introduction

HYDROGENATION OF A FAT is the largest single chemical reaction in the edible fat industry and may be considered to consist of a simple addition of hydrogen to the ethylenic linkage present in the unsaturated fatty acids. Actually the reaction is extremely complex and is the result of many simultaneous reactions. Not only is the hydrogen added to the ethylenic linkage, but also the ethylenic linkage is forced up and down the hydrocarbon chain of the fatty acid and may also be isomerized, that is, the shape of the molecule is changed and thus its physical properties are also. The catalyst used for the reaction not only catalyzes the addition of hydrogen but also these isomerization reactions to varying degrees. Thus the selection of the catalyst becomes very important since a complex set of reactions is being dealt with.

Since subsequent papers in this series will deal with the practices of hydrogenation as it is carried out in the industry, this report is concerned only with the catalysts used in the industry and some of their characteristics.

Catalysts which are used for hydrogenation can be classified in various ways. However, since there are only two metals, nickel and palladium, which have found any practical use in the field, they may be classified on the basis of the metal and also the method of reduction which is used to prepare the catalyst. Although palladium has not found wide use at the present in the edible fat and oil industry, it would seem that some effort is being made to use this catalyst. As will be seen later, this catalyst does offer some interesting possibilities. Therefore practically all of the hydrogenation is now carried out with the aid of nickel catalysts. These have, of course, found wide use not only in the edible field but also in the preparation of such inedible products as alcohols, amines, etc.

There are three ways in which nickel catalysts may be prepared. The first is the pyrolysis of a nickel formate. This is usually called the wet-reduction because it is carried out in a mixture of nickel formate and oil and thus is in a liquid state during the reduction. Nickel formate prepared from the reaction of formic acid or sodium formate with another nickel salt is mixed with an oil or fat and is heated; the decomposition products are either pulled off by the aid of a vacuum or allowed to escape in a carrier gas, usually hydrogen. After the formate has been heated to a temperature of about 240C and held at this temperature for some time (1 or 2 hr), the nickel formate is decomposed to a finely divided metallic nickel and is then an active catalyst. The fat which is present is hydrogenated and protects the catalyst from air. The mixture is usually flaked for shipment.

The other major way in which nickel catalysts are reduced is known as the dry-reduction method. To prepare a catalyst by this method, a nickel salt solution is absorbed on some type of carrier such as clay, alumina, or diatomaceous earth; then the material is dried and ground. The ground material is heated in a closed furnace in the presence of H_2 to about 500C. The supported nickel salt is reduced to black metallic nickel during the reduction. After the reduction is complete, the catalyst is quite pyrophoric so usually an inert gas is substituted for the hydrogen on the catalyst before the catalyst is exposed to the air. Thus the catalyst is stabilized and may be shipped without danger.

The third method of reducing nickel to prepare an active catalyst is by the reaction of a nickel aluminum alloy with concentrated sodium hydroxide. The aluminum dissolves in the caustic with the production of hydrogen, and the finely divided nickel is thus reduced by the hydrogen which is produced by the reaction of aluminum in the caustic. The soluble aluminum salts are washed from the nickel with water, and the catalyst is protected from the air by leaving it in a water slurry. This catalyst, known as Raney catalyst, has been used more in the preparation of fatty derivatives. It has not found wide use in the edible field.

Palladium catalysts are prepared by the absorption of a palladium solution on a carbon carrier with subsequent reaction. Most of this type of catalysts which is offered for sale at present contains either 1% or 5% palladium on carbon. Of course, the manufacturers will supply any concentration of metal on the catalyst carrier that is desired.

Although nickel and palladium are the prime hydrogenation catalysts, these may be mixed with other metals and thus the properties of the catalysts may be varied. For example, zirconium may be added to the nickel before reduction and the properties of the resulting catalyst may be different. Usually these trace materials are added to promote the activity of the catalysts.

Also some work has shown that the support used with the catalyst may affect the catalyst. For example, if titanium dioxide is used as a support, the catalyst may be somewhat more active than if an alumina or other oxides are used. It can be seen that there are many ramifications of catalysts preparation. Although catalyst preparation is not too complex a process, usually the fat processor will leave the preparation to catalyst manufacturers, who offer a wide variety of catalysts.

The hydrogenation of the unsaturated fatty acids, as shown in Figure 1, is a simplified version of the reaction. The reaction sequence of the hydrogenation of a mole of linolenic acid, the three double-bond acid, is the first double bond, hydrogenation, and production of linoleic and isolinoleic. These are then hydrogenated to oleic or elaidic (*trans*), which are then hydrogenated to stearic. Of course, as is shown, 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 which 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

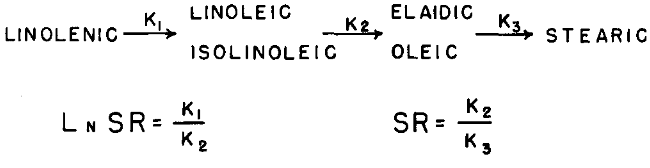

FIG. 1. Simplified reaction sequence of hydrogenation.

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[1] Presented at the AOCS Short Course, East Lansing, Mich., Aug. 29–Sept. 1, 1966.

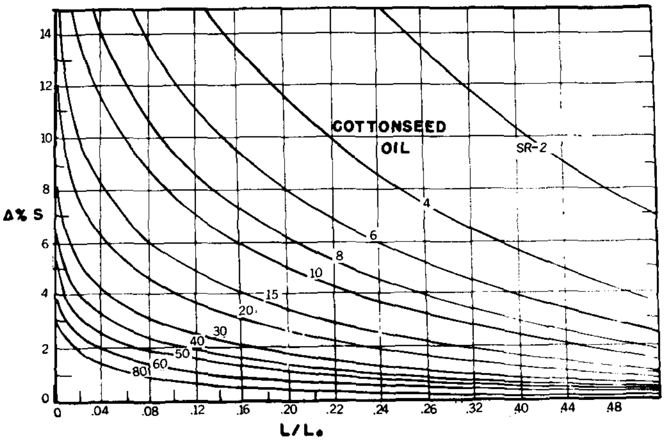

FIG. 2. Calculation of the selectivity ratio for the hydrogenation of cottonseed oil.

oil is complicated by the fact that not only is the most unsaturated molecule hydrogenating but at the same time all the others which 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 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. 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 or nonselective, and some word descriptions which were vague were used to describe the selectivity. Thus what one person may call 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. Lyle Albright of Purdue University (JAOCS, March 1965) published a number of graphs which have been found useful in assigning a selectivity number to a catalyst. Catalysts may be judged by this selectivity number. This selectivity number as defined in Albright's publication is simply the ratio of the reaction rates of the hydrogenation of linoleic acid compared with the hydrogenation of oleic acid.

As shown in Figure 1, 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 example, a selectivity ratio of 10 means that the linoleic acid is being hydrogenated at 10 times the rate of the oleic acid. A selectivity ratio of 50 would mean that the linoleic acid is hydrogenated at 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. When these values are known, they are applied to the graphs which were published in the original paper. For example, Figure 2 shows a graph for the calculation of the selectivity ratio of a cottonseed oil hydrogenation. In the original paper the y axis of the graph was shown as a delta IV, which means the IV drop attributable to the excess hydrogenation to stearic acid. However it has been found that the delta IV term is actually an increase in the amount of stearic which is formed during the hydrogenation.

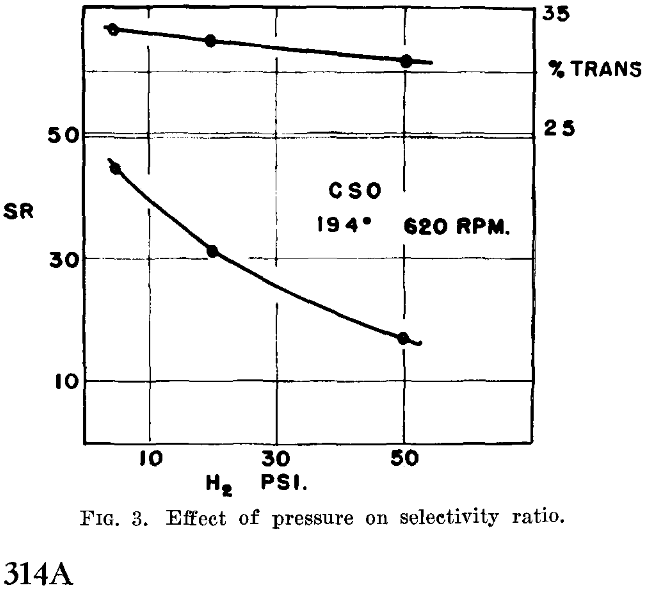

FIG. 3. Effect of pressure on selectivity ratio.

TABLE I
Hydrogenation of CSO
400F, 20 psi to 75 IV

Catalyst	1	2	3
Palmitic, %	21.8	21.8	21.8
Stearic, %	3.6	4.0	4.8
Oleic, %	62.3	60.8	60.7
Linoleic, %	11.6	11.9	11.3
trans, %	37.8	35.7	36.6
SR	60	50	32

The ratio of the starting and the final linoleic acid which is present in the final product compared with the amount of stearic acid that is formed gives the selectivity ratio. For example, if .24ths of the linoleic was hydrogenated and 6% stearic was formed during the reaction, the selectivity ratio would be about eight. This would mean that the linoleic acid was hydrogenated only eight times as fast as the oleic acid. As can be seen from the graph, if one has perfect selectivity, if, 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, secondly, that the *trans* or iso-oleic hydrogenates at the same rate as the oleic. These are simplifying assumptions and are probably valid, at least for use in this type of study.

To illustrate how this selectivity ratio may be used, Table I shows the results of hydrogenation under specific conditions of cottonseed oil to 75 IV by using three different catalysts. The fatty acid composition is as shown and as can be seen, the selectivity ratio of the three catalysts is quite different. Also the solids curve for the three products was different; the one with the most stearic, lowest selectivity, had the highest and slightly flatter solids curve. Also the cloud-point and capillary melting-point were higher. Thus the selectivity ratio, calculated from comparison of reaction rates, agrees with the old definition of selectivity, the lowest melting-point for a given iodine value. The catalyst with the highest selectivity may not necessarily be the best catalyst for the process or product that is being prepared. For example, if some stearic acid is desired in the product, then the catalyst would be used which gives a lower selectivity.

Also, the selectivity ratio does not correlate with the *trans* content. In several hundred hydrogenations which have been run by using many types of catalysts and conditions, no correlation between the selectivity ratio and the *trans* content has been found although one will find in the literature that these two are correlated. The only time that the selectivity ratio and the *trans* are correlated is when the same catalyst is used and the conditions are varied. Then one finds that usually the reaction conditions which gave the highest selectivity will also give the highest *trans* although this, again, may not be true in all cases.

It has been found that the wet-reduced formate catalysts usually give high selectivity ratios whereas the dry-reduced catalysts give somewhat lower selectivities. This has been the experience of the plant hydrogenations also. It does not mean that the wet-reduced catalysts are better for particular hydrogenations than the dry-reduced but only that the reactions are different and thus the products are different.

Figure 3 shows the effect of pressure on the selectivity ratio. For example, at five pounds of pressure a particular catalyst which was used in this study had a selectivity ratio of about 45. At 20 pounds of hydrogen pressure the selectivity ratio dropped to 30, but if 50 pounds

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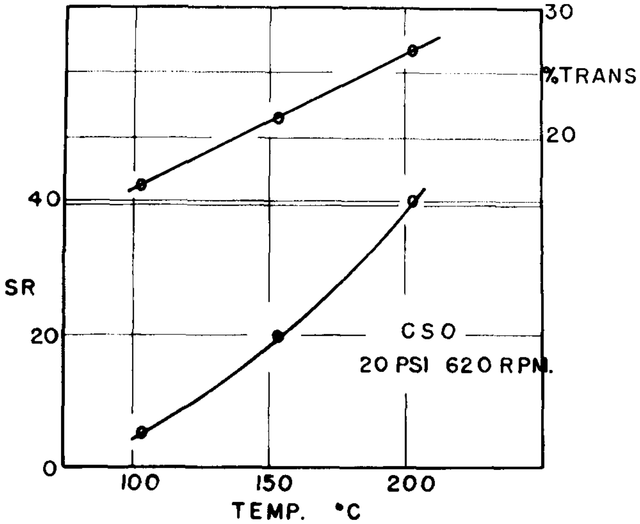

Fig. 4. Effect of temperature on selectivity ratio.

of pressure were used, the selectivity ratio was decreased to about 18. However *trans*, which was measured at an 80 IV level, dropped only from about 33% at five pounds of pressure down to 31% at 50 pounds of pressure. Thus the pressure effect on the *trans* was not great.

Figure 4 shows the effect of hydrogenation temperature on the selectivity ratio. Temperature has a great effect on the ratio. At 103° the selectivity ratio is about five, but if a temperature of 205° is used, then the selectivity ratio increases to about 40. Also temperature seems to have the greatest effect on the *trans* content, which was measured at 80 IV.

The catalyst concentration, although it is not shown in this study, has little effect on the selectivity ratio if the concentration is held within the economical boundaries of about .02% to about .1% nickel. The speed of the reaction, of course, is increased somewhat as the catalyst concentration is increased, but the selectivity ratio is affected very little. Of course, if the temperature and/or pressure of the reaction are increased, the over-all speed is increased and the individual reactions in the sequence are affected as well. However different catalysts cause different responses of the individual reaction. For example, increasing temperature may cause one catalyst to increase K_2 more than K_1 and K_3 whereas another catalyst would increase K_3 more than K_2.

Another reaction parameter which 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 mixture so that it may come in contact with the hydrogen and with the unsaturated carbon chains. Also the agitation must dissipate the heat of the reaction and not allow any over-heating or hot spots in the reaction.

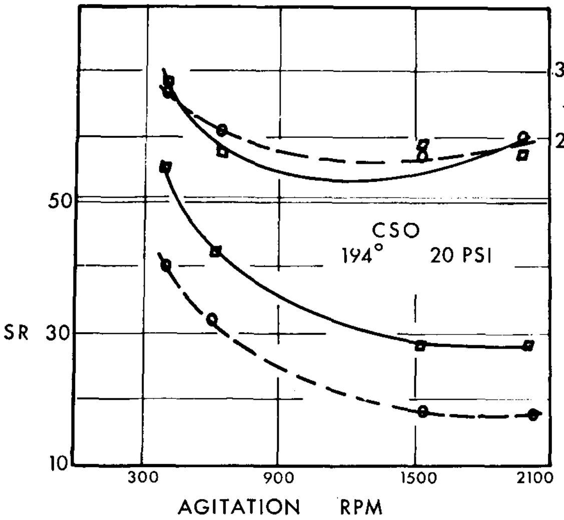

Fig. 5. Effect of agitation on selectivity ratio.

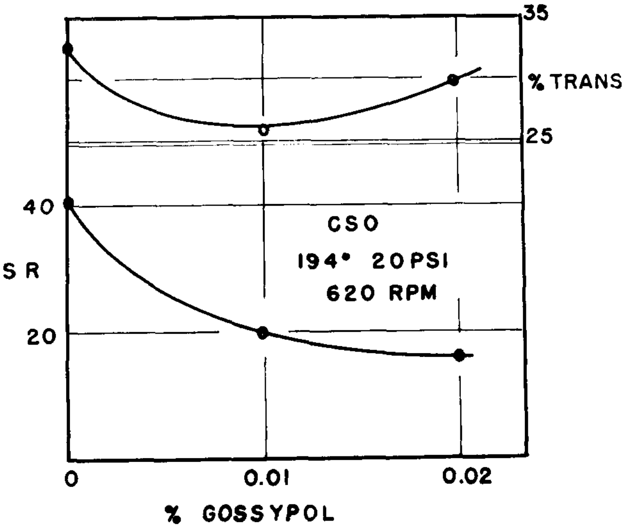

Fig. 6. Effect of gossypol on selectivity ratio.

Figure 5 shows the effect of the rate of agitation of a laboratory hydrogenator. The equipment was a Paar medium-pressure apparatus, using a single six-blade propeller on the agitator shaft. As shown, the increase in agitation decreased the selectivity ratio until any increase in agitation did not affect the reaction. In other words, at about 1,550 rpm the rate of agitation was enough so that all resistance to mass transfers was eliminated. The two lines shown are for two different catalysts and show that the agitation rate affects catalysts to about the same extent, depending upon their initial selectivity ratio. This change in the selectivity ratio with agitation furnishes a useful tool 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 which is needed to eliminate the resistance to mass transfer. Also the internal structure of each of the converters affects the agitation. To match small equip-

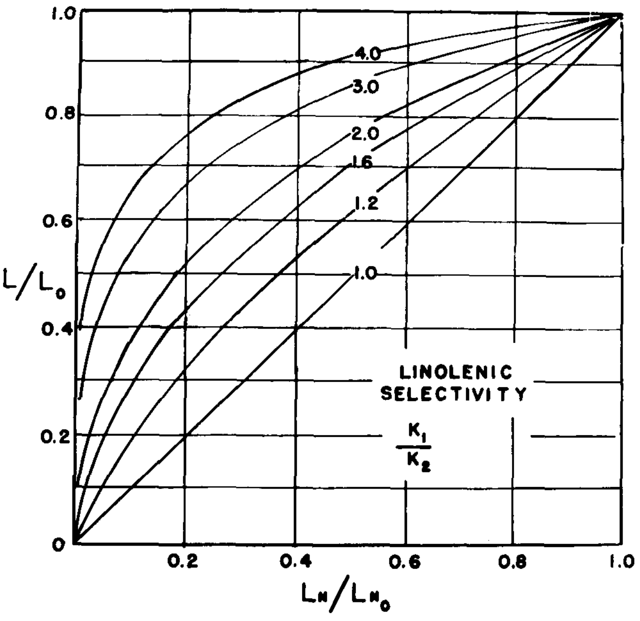

Fig. 7. Calculation of the linolenic selectivity ratio (Ln SR).

ment to the plant, the agitation rate of the small equipment is adjusted to obtain the same selectivity ratio by using the same oil, catalyst, temperature, and pressure as the plant. Usually, with two or three trial 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.

Not only do the reaction conditions and the catalyst determine the selectivity ratio but also many minor components in the oil affect the selectivity ratio. The most dramatic is the effect of gossypol on the hydrogenation of cottonseed oil. Figure 6 shows the change in selectivity ratio with an addition of small amounts of purified gossypol. The rate of the hydrogenation of cottonseed oil is not affected by the presence of gossypol but only the selectivity of the catalyst. Evidently the gossypol is absorbed on the catalyst in such a way that the over-all rate of the hydrogenation is not affected but the relative rates of the various reactions are. Many other materials which are present in oils affect the hydrogenation in a similar way.

The selectivity ratio is the ratio of the rate of linoleic hydrogenation to the oleic hydrogenation, but there is another important reaction involved in hydrogenation, and that is the hydrogenation of the linolenic acid which is present in soybean oil. The linolenic acid is believed to contribute to the flavor reversion of this oil so the primary aim of hydrogenation of soybean oil is to reduce the linolenic content as much as possible. Several schemes have been outlined to calculate the linolenic selectivity of a hydrogenation reaction or catalyst. A simple method, based on Albright's work, is shown in Figure 7 and compares the ratios of the beginning and ending linoleic and linolenic acids. The linolenic selectivity ratio or the ratio of the reaction rates of the hydrogenation of linolenic compared with the reaction rate of linoleic acid may be estimated from the calculated curves. These were calculated from the same equations which were used for the selectivity ratio. In all of the publications and hydrogenations with soybean oil the linolenic acid shows a reaction rate considerably higher than the linoleic acid. A selectivity ratio for linolenic acid of about two is the usual ratio for nickel catalysts. Surprisingly, the reaction conditions do not affect the linolenic selectivity to any great extent.

It was found also that palladium has a somewhat higher linolenic selectivity and shows the ratio to be about three whereas at the same time the linoleic selectivity or the SR of a palladium catalyst is somewhat lower than that of the nickel catalyst. Also, palladium forms much more *trans* than nickel under conditions to give the same SR. It can be seen that the type of catalyst affects the comparative speeds of the various reactions. Thus there is no one catalyst that is best for all products. It can be seen that the selection of the hydrogenation catalyst should be made only after a study of the reaction product which is desired, the particular equipment which is being used, and, of course, the type of oil as well as degree of refining because all of these things affect the catalyst and thus the product which is formed.

The use of the selectivity ratio in the future should make possible a better comparison of catalyst and reaction conditions. If this selectivity ratio is used in future publications, it will be possible to compare catalysts and to aid in the preparation of catalysts which will hydrogenate one single type of molecule over those others that are present in the mixture.

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• *Obituaries*

L. B. Parsons (1938, retired), died Feb. 28, 1968, in Ridgewood, N. J.

W. S. Singleton (1943), research chemist at the Southern Regional Research Laboratories, New Orleans, died recently, according to word received at Chicago headquarters.

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