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# The Effect of Deodorization Prior to Hydrogenation on the Development of Hydrogenation Odor in Fats[1]

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THE HYDROGENATION of refined and bleached oil for edible purposes is always accompanied by the formation in various degree of an odor and flavor that differ markedly from the odor and flavor of the natural oil. Although the exact source of hydrogenation odor has never been definitely established, there are several theories as to its origin. Lange (1) has postulated that the odor arises from the cleavage of unsaturated glycerides. Vakil (2) has suggested that the origin of hydrogenation flavor "must be traced to the formation of an intermediate product in the process itself since carefully refined and deodorized neutral oil gives rise to the flavor." According to Mielck (3), the odor might arise from ethers of long and short chain alcohols or from the hydrogenation of diglycerides to acetyl carbinol.

Even though careful deodorization of hydrogenated oils apparently removes completely the substances responsible for hydrogenation flavor, the bland oils sooner or later revert, and many samples develop a flavor resembling that of undeodorized oil. This suggests a possible relationship between hydrogenation flavor and reversion. The so-called reversion odors and flavors and their resemblance to hydrogenation odors and flavors are more noticeable with highly unsaturated oils, such as linseed and soybean, than with oils, such as cottonseed and peanut. The objective of this investigation was to find a method which would prevent the formation of hydrogenation odor and flavor and, if such a method could be found, to determine its relation to flavor stability.

Theoretically the mere addition of hydrogen to unsaturated fatty triglycerides in a pure form should result in the formation of no odor or flavor. Therefore it was decided to reinvestigate the work of Vakil (2) on the hydrogenation of deodorized oil and, if possible, to ascertain how the characteristic odor of hydrogenation is developed.

## Experimental

A sample of alkali-refined and bleached soybean oil was deodorized in glass equipment at 230°C. When the oil was hydrogenated the next day in an iron converter at 190°C. with 0.1% nickel catalyst, significant amounts of odor and flavor developed.

Next a sample of oil was deodorized and immediately hydrogenated in glass at 70–80°C., with 0.2% palladium catalyst (5% palladium on charcoal) to an iodine number of 95. The hardened oil had no odor or flavor characteristic of hydrogenation and received a flavor score of 9, using a flavor scoring system similar to that developed at the Northern Regional Research Laboratory (4). A flavor score of 9 represents an oil in which flavor is barely detectable, 8 a slight flavor, 7 a definite flavor, and 5 or 6 a rather strong flavor. An attempt to repeat this surprising result with nickel catalyst at 190°C. was not as successful, and the oil had traces of hydrogenation odor.

A portion of the same deodorized oil was autoxidized for 3 hrs. at 60°C. in the presence of light and then heated at 200°C. for 20 min. The reverted oil, which possessed a strong painty odor, was then hydrogenated in glass with palladium catalyst at 90°C. The characteristic odor and flavor of hydrogenation were very strong.

These preliminary results showed that the odor and flavor, which develop during hydrogenation, are in some way related to the reversion of soft soybean oil from the effects of oxygen and heat.

Therefore further experiments were conducted in which refined and bleached oil was deodorized for 4 hrs. at 230°C. in the presence of 0.005% citric acid and protected with a blanket of nitrogen prior to hydrogenation. The oils were then hydrogenated with palladium catalyst at 90–100°C. and 5 lbs. of hydrogen pressure to an iodine number of 74 in a black iron converter, which had been thoroughly cleaned to remove oxidized and polymerized fat, also in a stainless steel converter. The oils were then filtered, bleached, deodorized briefly by heating at 230°C., and cooled immediately.

Samples of the same refined and bleached oil with a peroxide value of 8.0 were hardened similarly as controls and deodorized in the usual way for 4 to 5 hrs. at 230°C. The extent of odor formation and the flavor stability of these oils are shown in Table I.

The results show that predeodorization, protection of the deodorized oil from autoxidation, and hydrogenation at a low temperature in a clean vessel practically eliminate the development of hydrogenation

TABLE I

Soybean Oil Hydrogenated With Palladium Catalyst at 90–100°C.

| | Stainless steel converter | | Black iron converter | |
|---|---|---|---|---|
| | Predeodorized | Control | Predeodorized | Control |
| Hydrogenation odor.... | Trace | Strong | None detected | Strong |
| Flavor of deodorized oil aged at 60°C. | | | | |
| Initial........................ | 9 | 9 | 9 | 9 |
| 1 day........................ | 9 | 8 | 9 | 7 |
| 2 days........................ | 8 | 7 | 9 | .... |
| 3 days........................ | 8 | 6 | 9 | 7 |
| 7 days........................ | 7 | 6 | 8 | 5 |

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odor and give hardened oil of high flavor stability.

When the preceding experiments were repeated with nickel catalyst at 190–200°C., essentially the same results were obtained except that it was more difficult to eliminate the formation of odor or flavor. However, with careful protection of the predeodorized oil as well as of the hydrogenator from atmospheric contamination, the formation of odor was reduced to a negligible amount as compared to controls. In addition, these experiments showed that, in general, the hydrogenation of deodorized oil proceeds at a more uniform rate and is more rapid than the hydrogenation of undeodorized oil. This effect is shown in Figure 1.

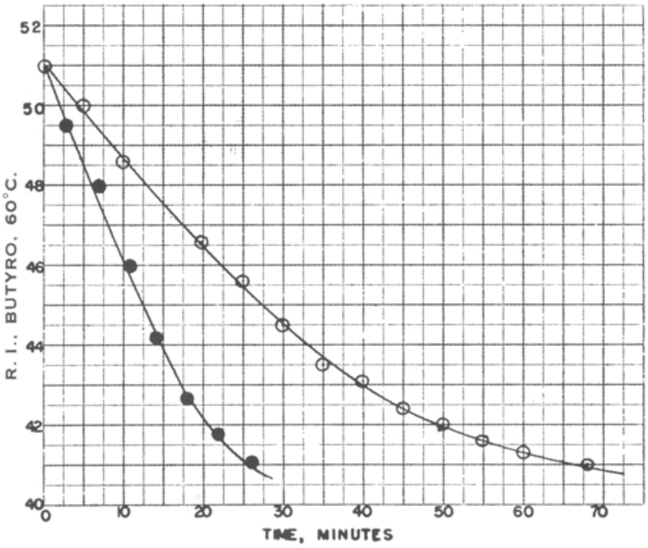

FIG. 1. Hydrogenation of soybean oil. 0.15% nickel catalyst, 200°C., 10 lb. ○ Refined and bleached. ● Refined, bleached, and deodorized. Stainless steel converter.

In order to check our laboratory experiments and the conception that hydrogenation odor and the flavor stability of hydrogenated oil are related to the presence of autoxidized substances in the soft oil at the time of its hydrogenation, four batches of alkali-refined and bleached oil of peroxide value 7.5 were processed as follows in a pilot plant. Each batch of 2,500 pounds was deodorized for 3 hrs. at 230°C. and transferred under nitrogen to a clean, evacuated hydrogenator which had been purged with nitrogen. The oil was then hydrogenated with nickel catalyst at 180–190°C. to an iodine number of 74. After cooling to 70°C., the converter was purged with nitrogen, and the oil was filtered in an open press. The oil at this stage was nearly bland and contained only slight amounts of odor and flavor. After bleaching at 77°C. in an open kettle, the oil was deodorized at 200°C. for 1 hr. and stabilized with 0.005% citric acid.

Four batches of the same refined and bleached oil were processed normally without nitrogen protection for controls. They were deodorized at 200°C. for 5 hrs. to remove the relatively strong hydrogenation odor which was present.

Mean flavor scores and peroxide values of the fresh and aged oils are shown in Table II. Each flavor score represents the average of 48 tastings since each batch of oil was sampled in duplicate by six judges.

TABLE II

Soybean Oil Hydrogenated With Nickel Catalyst at 190°C.

| | Predeodorized | Controls |
|---|---|---|
| Peroxide value prior to hydrogenation | 0.6 me./kg. | 7.5 |
| Hydrogenation odor | Trace | Definite |
| Flavor of deodorized oil aged at 60°C. | | |
| Initial | 8.9 | 8.3 |
| 3 days | 8.5 | 7.8 |
| 6 days | 7.6 | 6.6 |
| Flavor deterioration | 1.3 | 1.7 |
| Peroxide value of deodorized oil aged at 60°C. | | |
| Initial | 0.2 | 0.4 |
| 3 days | 0.6 | 0.9 |
| 6 days | 0.9 | 1.4 |

The peroxide values represent an average of eight determinations. Predeodorization of the soft soil reduced its peroxide value, almost eliminated the formation of hydrogenation odor, and resulted in hydrogenated oil of improved flavor and stability.

Statistical evaluation of these flavor scores showed that the differences are significant. Therefore scores of a similar magnitude could be expected in processing oil of a comparable quality.

## Discussion

It might appear that there is a definite relationship between the peroxide value prior to hydrogenation, odor formation, and flavor stability, but the effectiveness of predeodorization in preventing the formation of odor and improving the flavor stability of hydrogenated oil cannot be ascribed to the fact that peroxides and other products of autoxidation are decomposed. However, for oil which is properly handled at low temperatures and well protected from the effects of oxidation, the relationship of low peroxide value to low odor formation and high flavor stability undoubtedly holds, but it is not valid for oils which have come into contact with heat or other factors that promote the decomposition of peroxides.

The results obtained in these experiments can be explained on the basis that predeodorization removes from the oil certain compounds which are detrimental to the odor and flavor of hydrogenated oil. Autoxidation appears to play an important role in the formation of these compounds. The compounds known to be removed by deodorization are unstable peroxides, fatty acids, volatile monoglycerides, sterols, and the end-products of heat and oxidative degradation such as aldehydes, ketones, and alcohols. Deodorization also has the tendency to convert mono- and diglycerides to triglycerides. If the deodorized oil is hydrogenated before further oxidation or hydrolysis can occur, compounds such as those mentioned, some of which undoubtedly are susceptible to hydrogenation with a change in odor and chemical reactivity, are not present.

The advantages of hydrogenating an oil which is relatively free of impurities have been recognized by other investigators. As long ago as 1922 Bolton (5) recognized the importance of hydrogenating a highly purified oil with respect to catalyst contamination. Recently, during the course of our studies on the elimination of hydrogenation odor, Thurman (6) reported that the flavor of hydrogenated oil is improved if it is deodorized prior to hydrogenation. For the elimination of hydrogenation odor as well as maximum flavor stability, our results show that the deodorized oil must be protected from the effects of heat, light, and autoxidation so that it will be bland

and have a negligible peroxide value at the time of its hydrogenation. Furthermore it is also imperative to employ a hydrogenator which is free of oxidized and polymerized fat and maintained under an inert atmosphere when not in use. Otherwise the beneficial effects of predeodorization are lost.

Palladium catalyst is preferable for hydrogenating the deodorized oil because it is active at low temperatures, 40–100°C., where the rate of fat oxidation, decomposition, and splitting is low. In addition, palladium was found to be a very selective catalyst at low temperature. Since predeodorized oil hydrogenated with palladium catalyst at 90°C. contains only traces of odor and flavor, only a mild post-deodorization treatment is required. However the cost of palladium and its necessary recovery probably would outweigh the advantages on a practical basis.

Although it is believed that some of the compounds responsible for hydrogenation odor are involved in the reversion of hydrogenated oil, it should be realized that the evidence is indirect. However the presence of large quantities of autoxidized material in soft soybean oil definitely must bear a relationship to the flavor of the hydrogenated oil since, in general, predeodorization had its greatest effect on oil of poor quality, *i.e.*, aged or highly reverted oil.

## Summary

The direct precursors of hydrogenation odor are removed by steam deodorization. The primary precursors remain in the oil since the reversion of deodorized oil by autoxidation in the presence of light and heat forms certain compounds which again give rise to hydrogenation odor. Thus, in order to prevent the formation of hydrogenation odor, the deodorized oil must be protected from the effects of heat, light, and autoxidation, and hydrogenated in a unit which is free of residues from previous hydrogenations that were not carried out in a manner to prevent the formation of odor. The best results were obtained with palladium catalyst at temperatures below 90°C.

The high flavor stability of hydrogenated soybean oil which was deodorized and protected from autoxidation prior to hydrogenation indicates that certain compounds responsible for hydrogenation flavor may also be involved in flavor reversion.

## Acknowledgment

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# Problems of Selectivity in the Hydrogenation of Linoleic Acid Esters

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A MATHEMATICAL TREATMENT of the hydrogenation of linoleic esters is given, based on the assumption of distinct velocity ratio's $k_1 : k_2$ of the hydrogenation reactions of the starting material and intermediate monounsaturated esters.

Experimental data show that a number of high temperature hydrogenations (180° C., 1–100 at, Pt- and Ni-catalysts) conform to this scheme; they are characterized by a constant ratio of the hydrogenation velocities of linoleic and oleic acid esters. Low temperature hydrogenations (20–100°C., 0.1 at, Pt- and Ni-catalysts), in general, do not show such a constant ratio, probably due to the dominant influence of mass-transport phenomena of the reactants at lower temperatures. Data on hydrogenations of several fatty oils are considered in connection with the scheme mentioned above.

In the literature describing the hydrogenation of polyunsaturated fatty acids and their derivatives, difference is usually made between so-called selective and non-selective hydrogenations (1).

While in the former the formation of saturated products does not occur until complete transformation of the polyunsaturated molecules into monounsaturated ones is accomplished, in the latter no monounsaturates can be isolated during the reaction. These are immediately converted into the corresponding saturated end-products. These two reaction courses are the theoretical limits of possible ways of hydrogenation.

Another important course of hydrogenation is the one in which there is no preference for the formation or non-formation of certain definite intermediates. In this random hydrogenation, saturation of the double bonds of the starting material takes place according to the laws of probability, assuming that there is no mutual affection of the double bonds during the hydrogenation process.

In Figure 1 this is illustrated for linoleic acid esters. Linoleic and oleic acid (or the corresponding esters) are represented by L and O, respectively (iodine values 181.2 and 89.9); stearic acid, representing of course the final product of each complete hydrogenation, is given by point S in the diagram. The route L-O-S represents a completely "selective" course of the hydrogenation: the starting material is converted initially solely into monounsaturated esters without formation of saturated products. The route L-S, representing direct conversion of linoleic acid esters into the corresponding stearates without the intermediate formation of monounsaturates, gives the course of a non-selective hydrogenation.

The course of a random hydrogenation of linoleic esters is situated somewhere between the courses of