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

C. BOELHOUWER, J. SNELDERWAARD and H. I. WATERMAN, Technische Hogeschool, Laboratorium voor Chemische Technologie, Delft, Holland

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

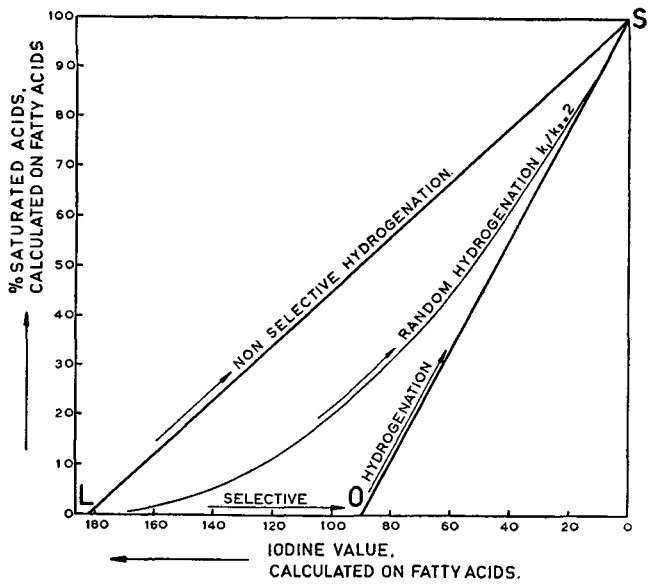

FIG. 1

completely selective and non-selective hydrogenations and can be easily calculated by taking into consideration the constant ratio $k_1 : k_2 = 2$ of the reaction velocities of consecutive hydrogenations of the starting material (a linoleic acid ester) and the intermediate monounsaturated ester.

When representing the reaction scheme by

$$\text{linoleic ester} + H_2 \xrightarrow{k_1} \text{oleic ester}$$

$$\text{oleic ester} + H_2 \xrightarrow{k_2} \text{stearic ester}$$

and representing the molecular concentrations of linoleic, oleic, and stearic acids by L, O, and S, respectively, the following equations hold:

$$-dL/dt = k_1 L$$
$$dS/dt = k_2 O$$
$$dO/dt = k_1 L - k_2 O$$

Assuming k_1 and k_2 constant during the hydrogenation processes and representing the ratio of the velocity constants $k_1 : k_2$ by a, it can be deduced on integration (2), assuming linoleic ester (molecular concentration L_o) as a starting material:

$$L = L_o\, p^a$$

$$O = \frac{a}{a-1} \cdot L_o\,(p - p^a)$$

$$S = L_o\left(1 + \frac{1}{a-1} \cdot p^a - \frac{a}{a-1} \cdot p\right)$$

in which $p = \sqrt[a]{e^{-k_1 t}}$.

With the aid of these equations it is possible to calculate, for different values of a, the course of the hydrogenation reactions in the diagram. In Figure 2 this has been done for values of a, varying from 1/8 up to 32, with the set of curves covering practically the whole diagram.

IT IS remarkable to see how far the course of hydrogenation experiments of linoleic acid esters under different conditions can be described by a constant ratio of the velocities of the consecutive reactions, and follows the curves of Figure 2.

A large number of reliable data concerning hydrogenation of linoleic esters was collected by Van Vlodrop (3). These data are represented in Figures 3 and 4. As follows from Figure 3, the experiments

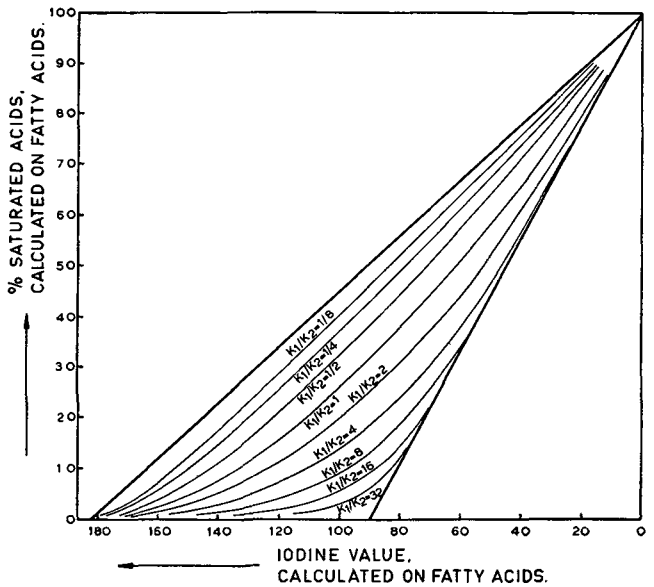

FIG. 2

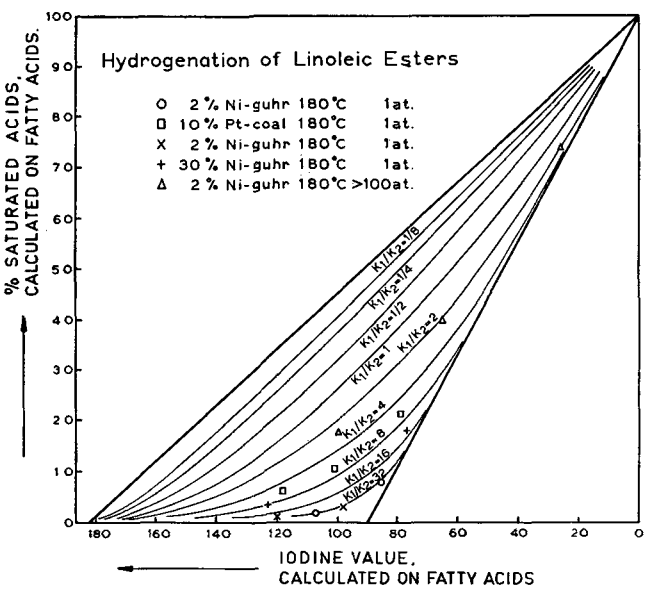

FIG. 3

at 180°C. (1–100 at, Ni- and Pt-catalysts) conform to the theoretical curves. These hydrogenations are characterized by a distinct constant ratio of the hydrogenation velocities of the starting linoleic ester and intermediate monounsaturates, which differs from $k_1 : k_2 = 2$ (low selectivity) to $k_1 : k_2 = 32$ (180° C., 1 at, high selectivity). This mainly depends on the extent of preferential adsorption of linoleic ester molecules on the surface of the catalyst; the random hydrogenation can be considered as a limit in this respect. In contrast with these experiments, hydrogenations of linoleic esters at lower temperatures de-

viate considerably from the calculated constant ratio curves (see Figure 4).

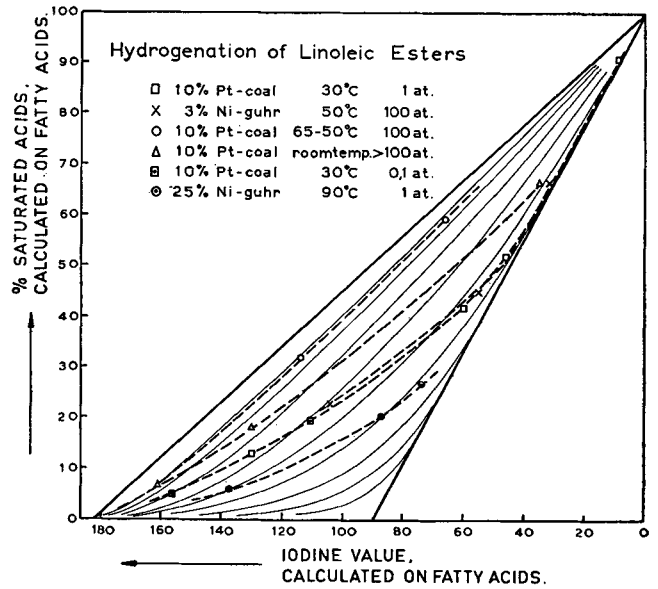

FIG. 4

Consequently there is a fundamental difference between low temperature and high temperature hydrogenation phenomena with nickel- and platinum-catalysts. Possibly transport phenomena of the reactants play a dominant part in the low temperature hydrogenation processes, and establishment of the adsorption and desorption equilibria at the catalyst surface is hampered. This might explain the increase of the ratio $k_1:k_2$ during the low temperature hydrogenations: formation of saturates being promoted in the first stages of the process by insufficient supply of linoleic esters to the catalyst surface.

In Figures 5–8 some data are given on the hydrogenation of linseed oil, soybean oil, arachis oil, and cod-liver oil with Ni-catalysts under different conditions (4, 5). The low pressure experiments were executed according to Normann (180°C., 1 at, hydrogen being introduced into the oil with extensive stirring) and Wilbuschewitsch (180°C., 1–5 at, a mixture of oil and catalyst being sprayed into an atmosphere of hydrogen). For the high pressure experiments a rotating autoclave was used. The more complicated composition of these oils, of course, hampers a direct comparison with the linoleic ester hydrogenation phenomena. It is possible however to correct the curves, representing the hydrogenation experiments, for the percentages of saturated fatty acids in the starting materials. This can be executed by a simple graphic subtraction, as is shown in Figures 5–8. As follows from these graphs, the corrected hydrogenation curves agree fairly well with the curves of linoleic ester hydrogenations under comparative conditions: the high temperature hydrogenations (140–180° C., 1–5, at) following approximately constant ratio curves, the low temperature experiments (30–70° C., > 100 at) on the contrary showing deviating courses.

An exception should only be made for experiments with colloidal nickel (see Figure 5). It is a well

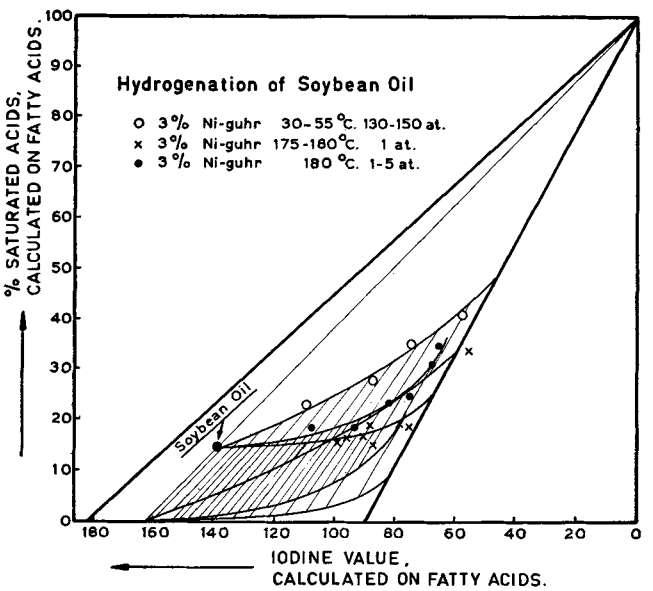

FIG. 6

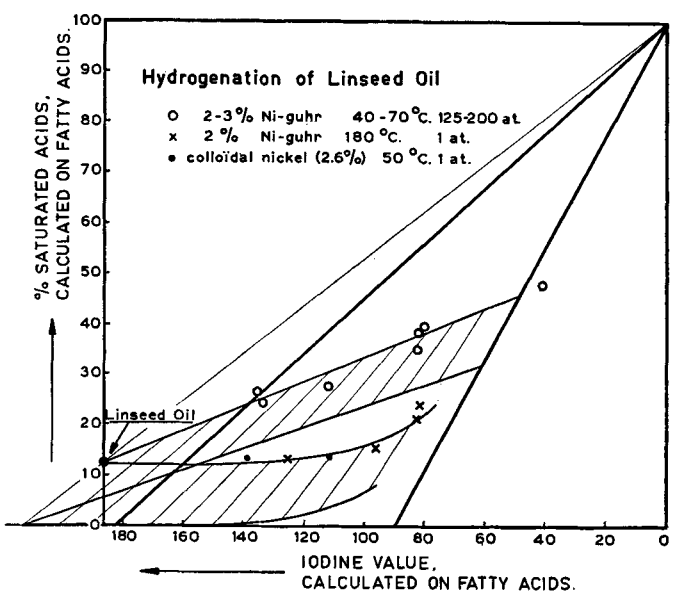

FIG. 5

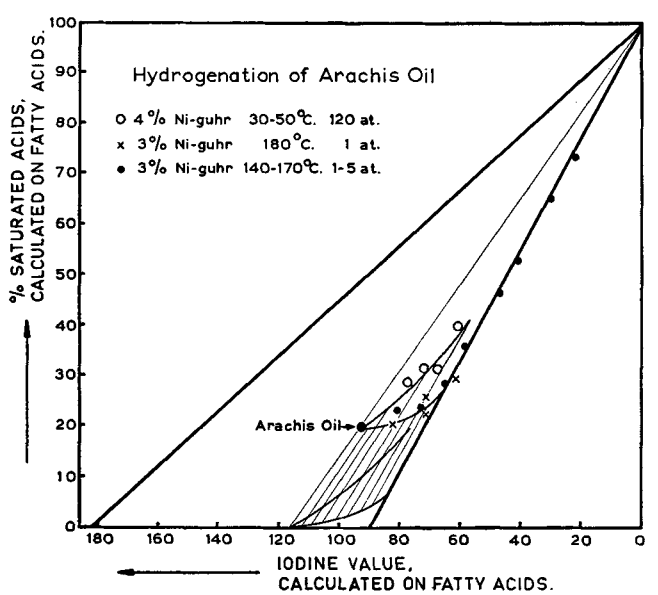

FIG. 7

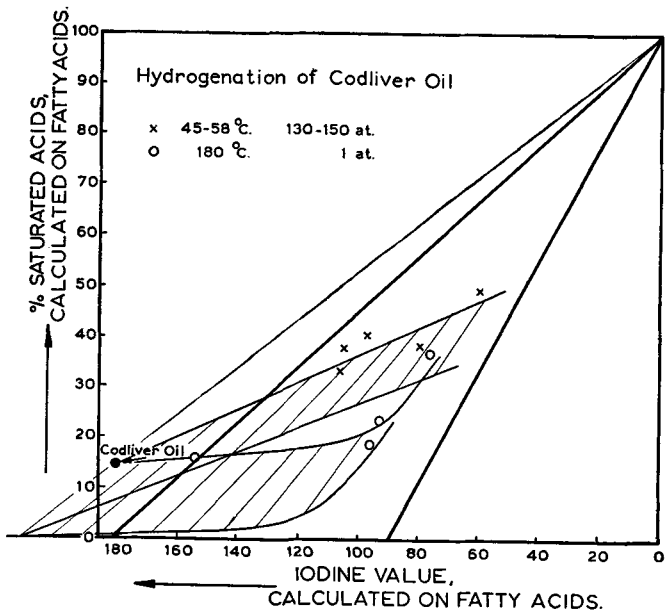

FIG. 8

known fact (5) that this catalyst shows a high selectivity in low temperature fatty oil hydrogenations (50°–60°C.).

From our considerations it can be concluded, in accordance with the opinion of Van Vlodrop (3), that, as a consequence of the extremely effective contact between the oil and this colloidal catalyst, no difficulties arise as to the transport of the reactants to and from the catalyst, notwithstanding a low reaction temperature.

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Constituent Fatty Acids of Salmon Egg Fat

R. M. KYTE, Fishery Products Laboratory,[1] Ketchikan, Alaska

THE FAT from salmon eggs has the very high iodine value of 220 and remains fluid at temperatures as low as —35°C. (3). These properties, and the fact that large quantities of salmon eggs are discarded each year in Alaska during the salmon canning season, have stimulated an interest in research on the constituent fatty acids of salmon egg fat.

The traditional method for determining the constituent fatty acids in a natural fat is that outlined by Hilditch (7). Hilditch and others have determined the constituent fatty acids of a great number of fats by this method (1, 2, 7). Many of the constituent fatty acids in fat reported in current literature are still determined in this manner (6, 12, 13, 14). The heating of the esters of highly unsaturated fatty acids, as is required in the vacuum distillation step of the Hilditch method however alters the heat-labile unsaturated compounds. The probable limitations of the Hilditch method, when analyzing unsaturated fats such as fish liver fats, were early recognized by Farmer and Vandenheuvel (5).

Hammond and Lundberg (8) recently published a correlation of refractive index, carbon chain length, and unsaturation for methyl esters of fatty acids. The purpose of the present paper is to report the constituent fatty acids in salmon egg fat determined by the Hilditch method and to indicate, from the correlation of Hammond and Lundberg, the extent of the alteration of the fatty acids that occurred in the course of analysis.

Experimental

Sample Collection. Thirty pounds of salmon eggs were collected during the normal commercial canning of pink salmon *(Oncorhynchus gorbuscha)* at the New England Fish Company at Ketchikan, Alaska. The eggs were taken at random during the butchering of one day's catch of fish. Portions of skeins of eggs from an estimated 250 fish were sampled. The eggs were well developed but still in a tight skein and had an average maturity of 2.5 on the scale of Davidson and Shostrom (4). The eggs were frozen at —29°C. in sealed cans and stored at —18°C. until used.

Fat Preparation. Fat was separated from the eggs by the dilute brine extraction method of Sinnhuber (16). The eggs were thawed and passed through a grist mill, which broke the egg membrane. The ground egg mass was then diluted with twice its weight of 4% salt (NaCl) solution warmed to 50°C. The mixture was gently stirred, then allowed to stand for 4 hrs. with the temperature maintained at 50°C. The fat phase was siphoned off and clarified by passing through a Sharples super-centrifuge.

This gentle method of separating the fat from the egg resulted in a fat the reactive unsaturated constituents of which were unaltered as indicated by a determined extinction coefficient of essentially zero at 233 mμ. This fat however represented only ⅓ of the total lipid in the egg and consisted essentially of fatty acid triglycerides. In a preliminary report (9) a comparison was given of the constituent fatty acids in the brine-extracted oil with those in the total lipid obtained by exhaustive solvent extraction.

Analytical Procedures. The Hilditch method consists essentially of a) a preliminary separation of the fatty acids into saturate and unsaturate fractions, b) vacuum distillation of the methyl esters of these fractions into subfractions of simple composition, c) determination of iodine value and saponification equivalent on each of the subfractions from the vacuum distillation, and d) calculation of the constituent fatty acids from these data.

[1] The Fishery Products Laboratory is operated jointly by the U. S. Fish and Wildlife Service and the Alaska Fisheries Experimental Commission.