Hydrogenation of Edible Oils

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ABSTRACT

The supply and demand of edible oils and fats is briefly reviewed, and certain trends, relevant for the application of fat modification techniques, are noted. The effect of hydrogenation conditions on a number of selectivity aspects in hydrogenation with nickel catalysts is explained in terms of mass transport effects for hydrogen and triglycerides. The effect of selectivity on stability and melting behavior is also discussed. The limitations of the existing hydrogenation process with nickel are pointed out, and possible extensions by use of other catalysts, such as sulphur poisoned nickel, copper, and chromium complexes, are mentioned. Some technological aspects of the process are briefly reviewed.

SUPPLY AND DEMAND OF EDIBLE FATS

Raw materials for edible fat products are of natural origin, and their supply is therefore subject to seasonal and climatic influences. Moreover, economic and political factors cause fluctuations in the supply and demand. The total supply, composed of a large number of different oils, shows a steady growth over the past 15 years, marginally in excess of the growth of world population (1) (Fig. 1). The supply of individual oils, the origin of which is much more localized for reasons of climate, soil, and tradition, fluctuates much more widely, as is shown in Figure 2 for nine major oils, comprising ca. 70% of world production.

Although in the present century the oils and fats market has become more and more international, the traditional consumption patterns in producing countries change only slowly. As a result, an important fraction (50-80%) of production is consumed locally. In the Philippines, for instance, coconut oil contributes 84% to the fat consumed; in Nigeria, 87% of fat consumption is palm and palmkernel oil; in Australia, 73% of fat consumption is animal fat. Local consumption tends to follow a steady pattern, with a steady growth, especially in developing countries, due to
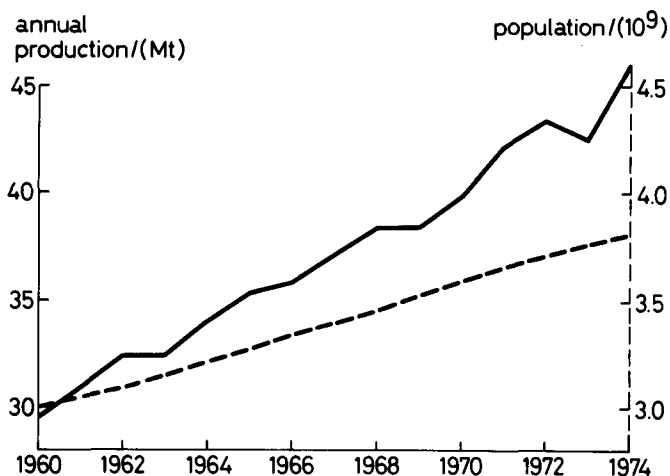
population increase. A larger share of local production is therefore retained in the country in years of poor harvest, so that fluctuations in production are magnified in export quantities (2,3). This effect is shown in Figure 3. The overall effect is that the composition of the total supply of fatty raw materials, as available in the world market, shows significant variations from one year to the next (Fig. 4).

It is evident that within the group of liquid vegetable oils the share of the less stable linolenic acid containing oils, soybean and rapeseed oils, is growing. This trend also extends over more recent years: soybean and rapeseed oil comprised 32% of total production of liquid vegetable oils in 1965, 40% in 1970, and 46% in 1974; the trend in exports is even more pronounced: 53% in 1965, 64% in 1970, 73% in 1974.

Obviously, the periodic fluctuations in availability have their effect on prices, as have other economic factors. Figure 5 shows prices over the past 8 years for three important vegetable oils. Although peaks and dips are
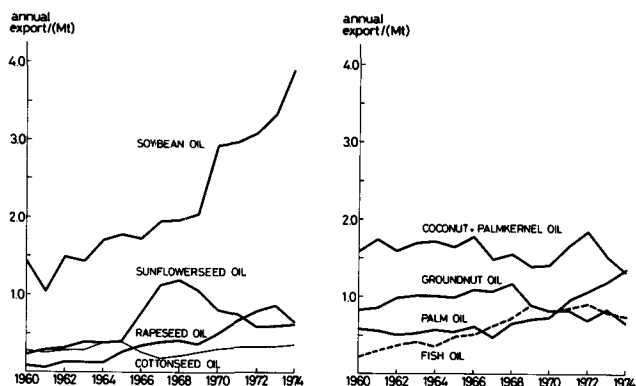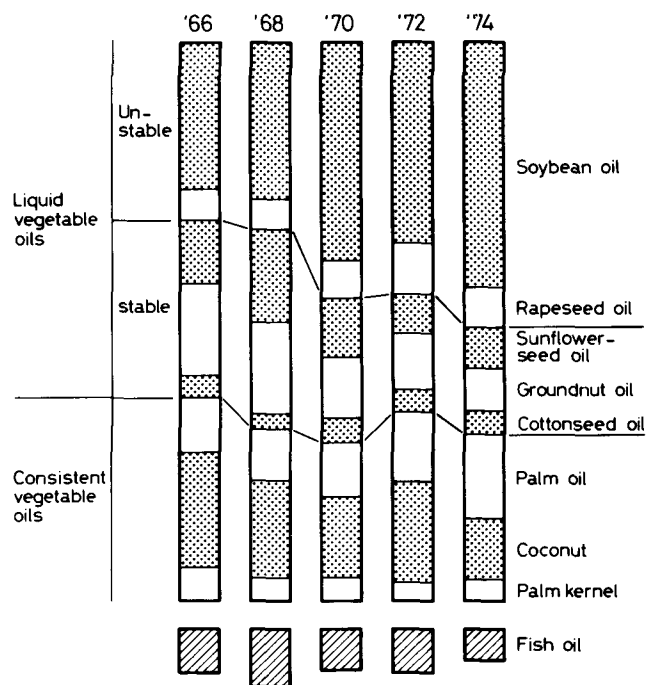

FIG. 2. World production of individual oils.

FIG. 3. World exports of oils and fats.

FIG. 1. World production of oils and fats (——) and world population(- - -).

FIG. 4. Composition of world exports.

FIG. 5. Price fluctuations for three vegetable oils.

sometimes slightly out of phase, there is a well-defined interaction between the prices of the three oils. For the two liquid ones, which should have a degree of interchangeability, this price correlation is not surprising. The fact that palm oil also follows the same pattern so closely is in part due to the use of fat modification techniques, which greatly enhance interchangeability.

On the demand side we note that an ever increasing proportion of finished products is sold as well-defined brands which the consumer expects to have constant characteristics throughout the seasons of the year and even from one year to the next. In many countries, these consumer goods are subject to price control, and allowed price adjustments generally lag behind the raw materials price development.

In general, we may say that the central problem in fat processing is to make products of constant and stable characteristics at a fixed price from a raw material supply that fluctuates in composition and price. In such a situation, flexibility in raw material choice is of vital importance; this is greatly enhanced by such fat modification techniques as hydrogenation, interesterification, and fractionation. We will deal with the most potent and versatile among them: hydrogenation.

AIMS AND BASIC CONCEPTS OF THE HYDROGENATION PROCESS

Hydrogenation eliminates part of the double bonds while a significant proportion of the remaining bonds is isomerized through cis/trans conversion and positional shift in the fatty acid chain. As a result of these chemical changes, a change in two important quality aspects occurs: the melting range is shifted to higher temperatures, and the stability to oxidation and flavor deterioration is improved. Originally, the former aspect was the primary aim of hydrogenation. The shift towards the production of softer margarines, and to some extent also the increasing availability of palm oil, make the improvement in stability now more important. Also, the trend that among the liquid oils the less stable ones are gaining in importance works in the same direction.

Hydrogenation is performed in a stirred tank reactor with the catalyst powder suspended in the oil. All oils contain impurities, which act as catalyst poisons. A sulphur
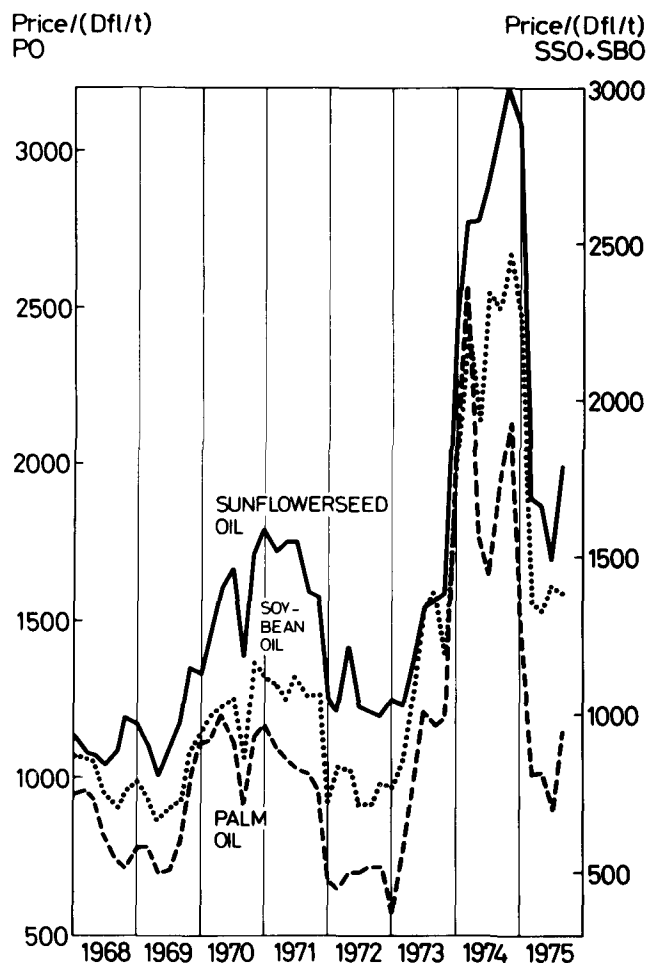
level of 5 mg/kg oil, a representative figure, poisons irreversibly 13 m² of nickel surface. For a catalyst to be easily filtered from the oil, particle size should be of the order of 5 μm. Solid nickel particles of this size have a specific surface area of ca. 0.15 m²/g. Thus, 87 g Ni/kg oil, or almost 9%, would be poisoned in one hydrogenation, which would be highly impractical and uneconomical. Therefore, all practical catalysts have porous particles with a large internal surface area. Nickel surface areas are of the order of 50-100 m²/g, reducing the amount of nickel poisoned to ca. 0.2 kg Ni/ton of oil.

Natural oils contain unsaturated fatty acids with one, two, and more double bonds; they differ in their reactivity in hydrogenation. For the present, we will consider only those with less than three double bonds. The course of reaction and its response to conditions is quite complex. To describe it in general terms, it is convenient to define three selectivity concepts (4):

Selectivity I, S_I (2), expresses the preference for linoleic acid over oleic acid hydrogenation. If this preference is high, hydrogenation of linoleic acid goes stepwise and formation of stearic acid is limited until linoleic acid has almost been eliminated.[1]

Specific isomerization, S_i, gives the number of *trans* double bonds formed per double bond hydrogenated.

S_I and S_i concern the fatty acid composition of the product.

Triglyceride selectivity, S_T, is a measure of the extent to which different fatty acid chains in one triglyceride molecule behave independently. If it is high, the distribution of fatty acids over the triglycerides remains random. If it is low, the fraction of *tristearate* formed in a product

[1]Generally speaking, the terms oleic acid, linoleic acid, stearic acid, etc., refer to them as glyceride esters, not as free acids.

$$L \xrightarrow{k_1} O \xrightarrow{k_2} S \quad S_I = k_1/k_2$$

—— = linoleic — — — = stearic ·······= oleic
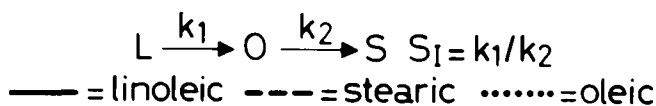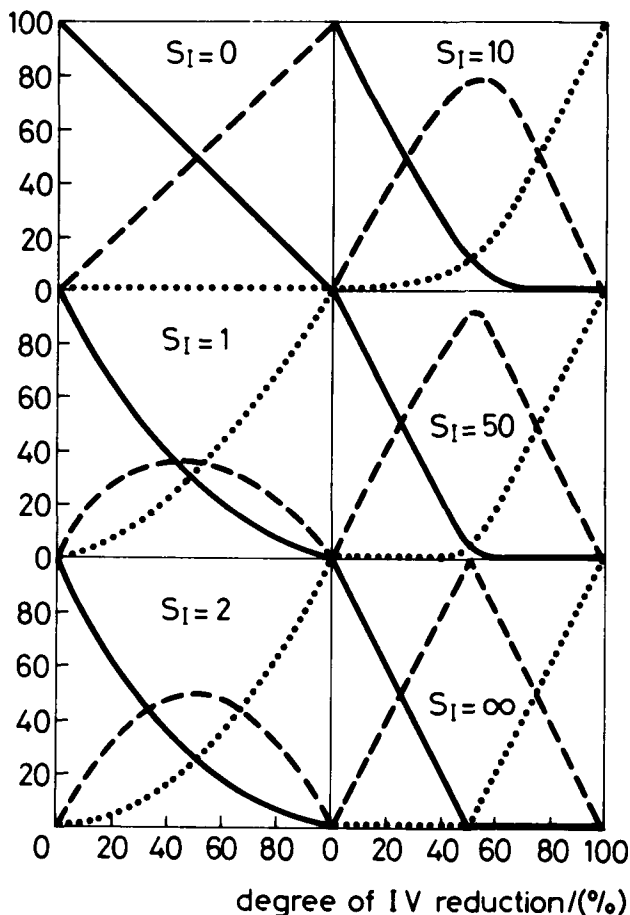
fatty acid
composition/(%)

FIG. 6. Theoretical composition curves for hydrogenation of linoleic esters. IV = iodine value.

with a fraction s of stearic acid exceeds s^3 and, in the extreme case, attains the value of s.

The elimination of linoleic acid and the formation of monoenoic and saturated acids can be described approximately with two consecutive pseudo first-order reactions:

$$L \xrightarrow{k_1} O \xrightarrow{k_2} S,$$
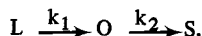
where L = linoleic acid, O = monoenoic acid, S = stearic acid. Thus, selectivity I can be defined as $S_I = k_1/k_2$.

In the course of a practical hydrogenation, S_I is not entirely invariant, but if we assume that it is constant, it yields a fair description of composition changes. Figure 6 illustrates effects to be expected. It gives calculated fatty acid compositions for the hydrogenation of linoleic esters for different values of S_I. The significance of the chosen values is as follows:

$S_I = 0$: All molecules react straight through to stearic acid. This situation is approached in hydrogenation with platinum catalysts at low temperature and very high pressure.

$S_I = 1$: Equal reaction chance for linoleic and oleic acid.

$S_I = 2$: Equal reaction chance per double bond: linoleic acid is twice as reactive as oleic acid.

a: Perfect triglyceride selectivity $S_3 = s^3$
b: Lowest possible triglyceride selectivity $S_3 = s$

$S_T = \dfrac{s - S^3}{s - s^3}$ equals 1 on curve a, 0 on curve b, 0.5 on curve c
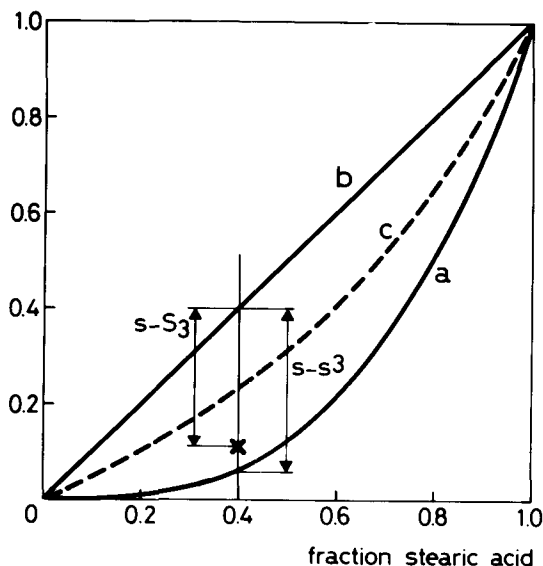
fraction tristearate

FIG. 7. Definition of triglyceride selectivity, S_T.

$S_I = \infty$: Stearic acid formation is inhibited. This case is approached in hydrogenation with copper catalyst.

Intermediate values, generally between 5 and 100, are obtained with nickel catalysts.

Figure 6 shows that at low values of S_I stearic acid formation starts from the very beginning, whereas at high values of S_I its formation is held back until the linoleic acid is almost eliminated. The concentration of monoenoic acid goes through a maximum, which reaches higher values at high selectivity.

The triglyceride selectivity is much more difficult to express in quantitative terms. If the triglyceride composition of the product is determined, we can express S_T as the degree of nonrandomness of this composition. The situation is visualized in Figure 7, where the solid lines give the extreme cases of $S_3 = s^3$ (high S_T) and $S_3 = s$ (low S_T). The expression

$$S_T = (s - S_3)/(s - s^3)$$

gives a measure of the degree of approach to the ideal curve, where $S_T = 1$.

EFFECT OF CONDITIONS AND TYPE OF CATALYST ON SELECTIVITY AND PRODUCT CHARACTERISTICS

Edible oil hydrogenation occurs necessarily in a three-phase system: solid catalyst, nonvolatile liquid triglyceride, and hydrogen gas with a limited solubility in the oil. Mass transport between the phases is of great importance since it determines to a large extent the actual concentrations of the reactants near the catalyst surface and these in turn govern the rate and selectivity of the reaction. We will consider both hydrogen transport and triglyceride transport.

Hydrogen Transport and Concentration (5)

Hydrogen, dispersed as bubbles, has to dissolve in the oil to reach the catalyst surface (Fig. 8). The bubbles, moving

Hydrogen   Oil   Catalyst
bubble   bulk   particle

| gas bubble | bubble film | oil bulk | catalyst film | catalyst pores | nickel surface |

Hydrogen con-   Oil composition   Situation here
centration is   can only be mea-   is decisive for
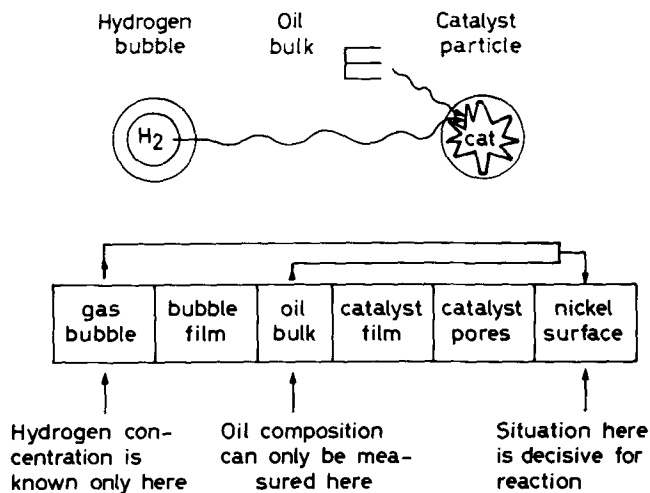known only here   sured here   reaction

FIG. 8. Mass transport in fatty oil hydrogenation. Six regions in a catalytic hydrogenation reactor.
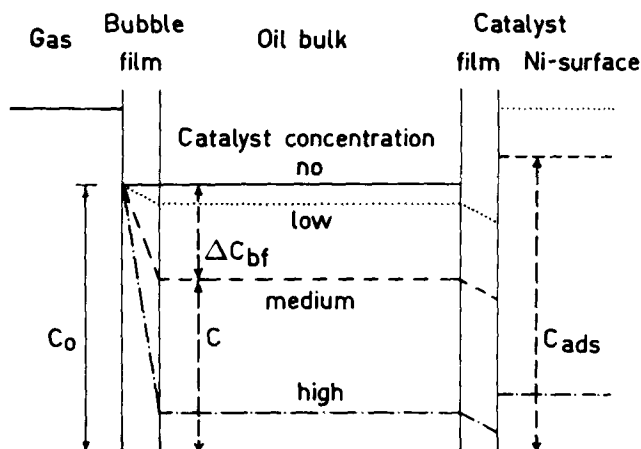
FIG. 9. Concentrations of dissolved hydrogen in oil (gas bubbling through stirred oil).

		Effect on		
	Increase of	H_2 conc.	S_l	S_i
Increases supply	Pressure	+	−	−
	Stirring intensity	+	−	−
	Temperature	−	+	+
Increases demand	Catalyst amount	−	+	+
	Catalyst activity	−	+	+
	Unsaturation of oil	−	+	+

FIG. 10. Influence of process conditions on dissolved hydrogen concentration near catalyst surface and on selectivities S_l and S_i.

through the oil in turbulent movement, are surrounded by a stagnant oil layer through which the dissolved hydrogen must pass by molecular diffusion. It will then reach the stagnant oil surrounding the catalyst particles and diffuse to the nickel surface, on which it is adsorbed as hydrogen atoms. It can now react with the unsaturated molecules.

Diffusional transport across the two stagnant oil films requires concentration gradients proportional to the rate of transport, which equals the rate of hydrogenation. In Figure 9, the hydrogen concentration across the system is shown for different levels of catalyst. The higher the catalyst level, the higher the rate of hydrogenation and the steeper the concentration gradients. The actual concentration of dissolved hydrogen near the nickel is only a fraction of the saturation concentration at the applied gas pressure. At high catalyst levels it can even approach zero. We can now predict how this concentration will respond to different reaction conditions. We already saw that it will fall with increasing catalyst concentration and the same will hold for higher catalyst activity. Increased stirring intensity will create a finer dispersion of hydrogen bubbles in the oil, a larger interfacial area across which diffusion must take place, so that the required gradient will be smaller: the concentration of dissolved hydrogen will accordingly be larger. A higher hydrogen pressure will have the same overall effect by proportionally increasing all concentrations in Figure 9. Increasing the temperature will have a much more accelerating effect on the chemical process on the nickel surface than on the physical transport processes. Demand will increase more than supply, and a depletion of the

dissolved hydrogen concentration near the nickel surface will result.

It is striking that the same conditions which lower the hydrogen concentration near the catalyst surface at the same time increase S_l and S_i (Fig. 10). To understand this, we may reason as follows. A high concentration of dissolved hydrogen near the catalyst will be reflected in a high coverage of the nickel surface with adsorbed hydrogen. We have demonstrated conclusively (6,7) that the selectivity is caused by the polyunsaturated fatty acids being more strongly bonded to the nickel surface than the monoenoic acids, so that the former monopolize the surface as long as they remain in significant concentration in the oil. How then does the degree of hydrogen occupation on the nickel surface affect the difference in bonding strength of polyunsaturated and monounsaturated fatty acids? Initially, either type of acid approaching the nickel surface will be bonded with one double bond, i.e., two carbon atoms, to the surface. If the hydrogen coverage is high, fast hydrogenation will occur on the adsorbed double bond. Selectivity will be low. A high proportion will be converted into cis-monoenoic acid, so that the specific isomerization is also low. If, however, the hydrogen coverage is low, an adsorbed linoleic acid moiety will find the time to split off a hydrogen atom from its reactive methylene group, thus becoming bonded with three carbon atoms to the nickel. The second double bond is now close to the nickel surface and can be bonded to it. It is clear that if this situation prevails, the bonding strength of oleic and linoleic acid becomes vastly different, resulting in a monopolization of the surface by adsorbed linoleic acid. Eventually, the adsorbed linoleic acid will take up a hydrogen atom, but this will probably occur at one of the ends of the pentabonded system, yielding the adsorbed form of the conjugated 9,11- or 10,12-octadecadienoic acid. Under these conditions, some conjugated acid is found in the hydrogenated product. Also, the double bond distribution, in both the cis and the trans fraction in the monoenes, is in agreement with this assumption (5).

The trans acids formed in the initial phase, as long as sufficient linoleic acid is present, are almost exclusively derived from the linoleic acid, since the oleic acid initially present is kept away from the surface and is neither hydrogenated nor isomerized.

Triglyceride Transport and Concentration (8)

We have seen that the catalyst particles are necessarily porous and that the pore system introduces the problem of diffusional transport of the large triglyceride molecules into and out of the pores. If these are long and narrow, diffusion is slow and significant concentration gradients are set up along the pores. The intermediate products—oleic and isolinoleic acids—build up inside the pore while polyunsaturated acids are depleted; the composition inside the pore runs ahead of that in the liquid (Fig. 11). Since the nickel surface does not "see" any polyunsaturated acid, there is no monopolization of the nickel surface either;
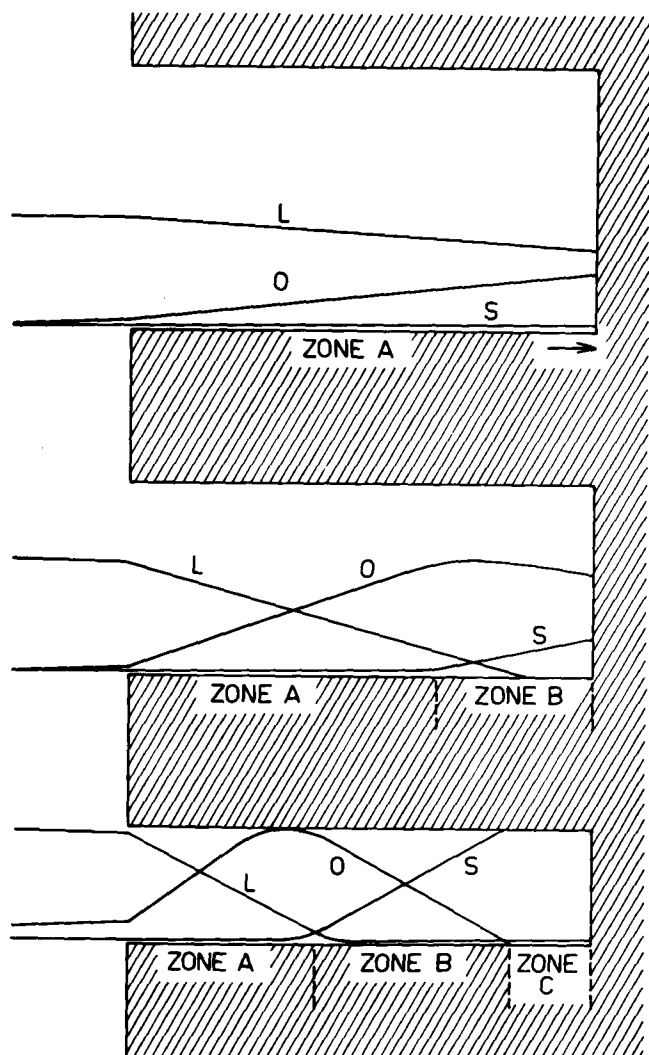
FIG. 11. Reactant concentration gradients in pores of different widths. In zone A, selective hydrogenation takes place. In zone B, stearic acid is formed. Zone C "sees" only stearic acid and does not contribute to the activity.

early in the hydrogenation, saturated acids and triglycerides are formed: low selectivity I and low triglyceride selectivity. In the extreme case, the molecules which do enter the pores are converted into tristearate, $S_I = 0$ (Fig. 6) and also $S_T = 0$: the fraction of tristearate in the product equals fraction s of stearic acid.

Also, the hydrogen concentration has a bearing on the pore transport effects. At high hydrogen concentrations (high pressure, intense stirring, low temperature, low catalyst level), the hydrogenation rate in a pore is increased and the triglyceride concentration gradients become steeper, with depression of selectivities S_I, S_T, and S_j.

The combined effect of transport limitation for both hydrogen and triglycerides satisfactorily explains the observed response of the different selectivity aspects to hydrogenation conditions. We will now consider how these selectivities reflect themselves in the product properties.

Effect of Selectivity on Melting Behavior

All fats are complex mixtures and have melting ranges which can be characterized by the SCI-temperature curve, a curve in which SCI (solid content index) is the percentage solid phase as determined by dilatometry or pulse NMR (nuclear magnetic resonance). The requirements regarding melting behavior differ from different classes of final product (4); we will limit ourselves to some salient points.

For most products, and particularly for margarines, confectionery fats, and cream fillings, it is desirable that the SCI is close to zero at body temperature, since solid fat
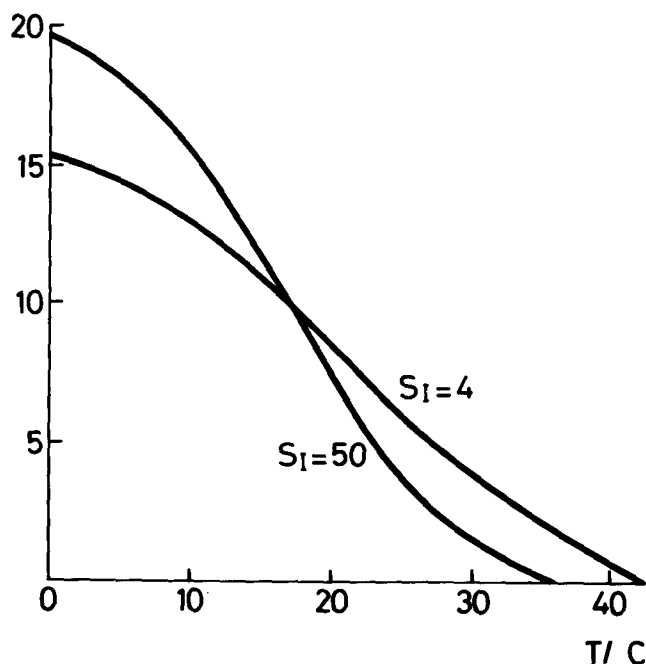

FIG. 12. SCI-temperature curves for soybean oil hydrogenated to iodine value 95 under conditions of high selectivity ($S_I = 50$) and of low selectivity ($S_I = 4$).

gives an unpleasant sensation in the mouth. Especially tristearate (S_3) and distearate-elaidate (S_2E) contribute to SCI at 37 C. For the same group of products, a cooling effect in the mouth is a desirable feature; it occurs if a large fraction of the fat melts between ambient and body temperature. Mainly E_3, SE_2, S_2O, and SOE contribute to the SCI in this temperature range. These fats are clearly intermediate products in hydrogenation, and high values for S_I, S_T, and S_i promote their formation and simultaneously limit the formation of undesired high melting triglycerides.

For bakery fats, on the other hand, some high melting triglycerides aid the structuring of the dough and dough stability in the initial stages of baking. For these products, a less selective hydrogenation may be desirable.

For frying oils, appearance and oral response of the fried product again makes the presence of high melting triglycerides unwanted, which makes high selectivity desirable.

For table oils, which should remain clear in the refrigerator, the SCI at 5 C should be as low as possible. For insufficiently stable oils, e.g., soybean oil, a slight hydrogenation is sometimes applied to improve stability. Generally, the resulting SCI at 5 C is then too high and winterization must be applied. Even then, high selectivity will keep the SCI low for a given iodine value reduction, which will improve the winterization yield.

It is impossible in the scope of this paper to substantiate all statements with data considering the large variety of raw materials and possible products. Therefore, we will limit ourselves to one illustrative example. In Figure 12, the SCI-temperature curves for the hydrogenation of soybean oil under conditions of high ($S_I = 50$) and low ($S_I = 4$) selectivity are shown. In Figure 13, we further show what is attainable and what is not. The striated areas indicate what is accessible with presently available means. The narrowly striated area contains the useful products. The more selective the hydrogenation, the further to the right the SCI 20/30 point is located. The straight line on the left is that for entire lack of selectivity.

solid-content index (30 C)
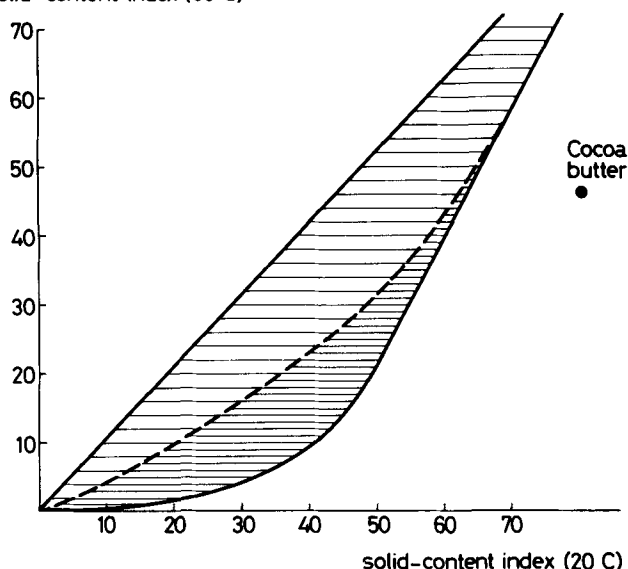
solid-content index (20 C)

FIG. 13. Hydrogenated products from soybean oil, accessible by present-day methods. Solids content index at 20 and 30 C. For comparison, the SCI 20/30 for cocoa butter is also given.

Effect of Selectivity on Product Stability

The flavor stability of oils is a very complex problem. Off-flavor development is due to oxidative breakdown, which generates volatile products, notably aldehydes from the nonvolatile triglycerides. The first point of attack of autoxidation is on the reactive methylene groups between the double bonds in the chain. Thus, the oxidation rate will increase steeply with the degree of unsaturation. The picture is complicated by the possible presence of certain trace components. Metals such as copper, iron, and manganese have prooxidant activity even in low concentrations. Certain oxidation products have an autocatalytic effect, so that the previous history of the oil is important. Components like tocopherols have antioxidant activity and retard the onset of oxidation. The human sensing organs are not equally sensitive to all volatile oxidation products, which complicates the link between the state of oxidation and the off-flavor level. It is virtually impossible to give rules, with one exception: unsaturated aldehydes generally have more pungent flavors than saturated ones. Obviously, the chance of splitting off an unsaturated aldehyde increases progressively with the number of double bonds in the chain. Accordingly, the presence of linolenic acid in an oil is detrimental to the stability, and more highly unsaturated acids, as present in marine oils, cause these oils to be highly unstable.

It will be clear that preferential elimination of polyunsaturated acids, as is achieved in selective hydrogenation, will lower the oxidation rate and also the chance of unsaturated aldehydes being formed in autoxidation. Thus, selectivity in hydrogenation should improve the flavor stability, which if often does. That this is not a universal truth is caused by the conditions for high selectivity I, also tending to promote isomerization. Sometimes, selectively hydrogenated products have a characteristic hardening off-flavor, which is due to the presence of specific precursor acids, which on oxidation yield very pungent unsaturated aldehydes (9). These acids, formed in hydrogenation, sometimes have two double bonds separated by more than one methylene group, so that the mechanism for their preferential hydrogenation is ineffective. Especially if one of the double bonds is in *trans*-configuration, the acid is a hardening flavor precursor. As a result of these complexities, it is impossible to formulate hard and fast rules on how to hydrogenate in order to attain the most stable product in all cases.

Prevention of Undesired Reactions (10)

From what has been said on the effect of selectivity on melting behavior and on flavor stability, it is clear that in many cases high selectivity is desirable. We have further shown that selectivity can be promoted by choosing conditions which induce a low hydrogen concentration on the catalyst. In the extreme case, formation of conjugated intermediates on the nickel surface is favored, but their elimination by hydrogenation is slow due to lack of hydrogen. The conjugated intermediates then have a long residence time on the nickel surface and may undergo undesirable side reactions: polymerization and cyclization. The chance of these reactions occurring is largest with highly unsaturated oils and at high temperature. A method has been worked out for their prevention, consisting of keeping the reaction temperature below 150 C in the first stage of the hydrogenation, where, due to the high content of polyunsaturated acids, selectivity is high anyhow.

TECHNOLOGICAL ASPECTS OF EDIBLE OIL HYDROGENATION

Materials

To prevent catalyst poisoning, which may result in slow reaction, high catalyst consumption, and selectivity depression, the oils should be carefully refined, which generally involves desliming, alkali neutralization, and earth bleaching. The latter step can sometimes be omitted. The hydrogen gas should be of high purity, 99.5%. Inert gases accumulate in the system as the hydrogen is consumed and lower the actual hydrogen partial pressure. Carbon monoxide, hydrogen sulfide, and, to a lesser degree, water vapor act as catalyst poisons and should be absent. Hydrogen of required purity can be obtained by water electrolysis for smaller plants or by steam reforming of hydrocarbons for larger installations. The latter process, if on adequate scale, is much more economical. Nickel catalysts can be obtained commercially, generally in reduced active form, protected against oxidation in hydrogenated fat, as flakes or granules for easy handling. Copper catalysts can also be obtained commercially as a dry powder, not yet in active form. At hydrogenation temperature, reduction and activation by hydrogen occur in the oil in the autoclave.

Procedure

The dry, prerefined oil is pumped to the autoclave. Part of the charge is mixed with the catalyst in a heated mixing vat and then introduced into the autoclave. Safety precautions should be observed to prevent occurrence of explosive mixtures inside the autoclave or in the factory at any stage of the protein. With running stirrer, the charge is heated by steam, and at a temperature of 120 C hydrogen is supplied. When the desired amount of hydrogenation is attained, the charge is cooled to < 100 C and filtered. The filtering oil may contain nickel—as much as 10 mg/kg in suspended or dissolved form. After postrefining, this level should be < 0.1 mg/kg. The catalyst from the filter press is recirculated for reuse via the catalyst mixing vat. Various procedures for reuse and addition of fresh catalyst are in use. Too much recirculation leads to impractically long filtration times.

Batch Hydrogenation Equipment

Due to the variation in raw materials and desired end products, application of continuous hydrogenation remains limited; therefore, most hydrogenation is done in batch autoclaves. These are cylindrical pressure vessels for batch sizes of 5-20 tons. Height diameter ratio is ca. 2, for the liquid charge ca. 1.5. The vessel is equipped with a central stirrer axis, bearing two or more agitators, preferably of the turbine type. The filling height should be such that the top stirrer is not submerged too deeply, so that hydrogen gas from the headspace is sucked into the oil and dispersed as

fine bubbles. Pipe coils serve for steam-heating the charge before hydrogenation and for cooling it with water to eliminate the considerable heat of reaction and to bring it to filtration temperature when the end point is reached. Preferably an automatic temperature control system regulates the cooling-water supply.

Two types of arrangement are in common use: gas circulation and dead-end regime. In either case, the hydrogen is fed to a sparger below the bottom agitator. In the circulation system, gas from the top of the vessel passes via a separator for entrained oil, optionally a scrubber, and circulation pump, back to the gas inlet at the bottom. Fresh gas to make up for consumption is supplied to the loop. In the dead-end system, there is no circulation loop; the system relies on the efficiency of the agitators to disperse the gas passing upwards and to suck back gas from the headspace to create a large gas oil interface.

The dead-end system has the advantage of being mechanically simple, and, provided due attention is paid to purity of materials and filling height, it can work exceedingly well. The circulation system is less critical with respect to purity, dryness of gas and oil, and filling height, but requires more maintenance due to fouling and wear of the circulation system. Choice of conditions and consequently requirements to be met by the equipment are a compromise, mainly governed by the exothermic heat of reaction and the selectivity to be attained. As evolves from earlier explanations, one may in principle keep selectivity constant by a simultaneous increase of catalyst amount and hydrogen pressure and/or stirring intensity. These measures all increase the rate, and very soon the heat liberated imposes a practical limit. In larger autoclaves, it is difficult to install more than 4-5 m^2 cooling surface per ton capacity. Reasonably attainable stirring power take-up is of the order of 2 kW/ton. With the heat transfer coefficient prevailing, the maximum allowed reaction rate is ca. 130 units. IV/hr at a temperature of 180 C, but considerably less at lower temperatures. Thus, practically applied pressures range from 1 to 6 atm gauge, so that autoclaves are designed for maximum pressures of 10 atm gauge. After completion, the charge is filtered in a plate and frame filter press. More sophisticated self-discharging separation devices have been tried but generally fail to filter out the finest catalyst particles. Various mechanized versions of filter press are obtainable, which are easier to operate. Still, press cleaning remains labor-intensive. A conveyor below the press brings the catalyst back to the mixing vat.

Continuous Hydrogenation

In principle, continuous hydrogenation has a number of potential advantages. In batch operation, the autoclave serves also as preheater and as waiting tank for filtration, so that actual utilization is low. In continuous processing, preheating and postcooling can be done in part via mutual heat exchange, affording heat economy and better utilization of equipment. There is, however, the danger of fouling by catalyst deposition. The most real advantage is that, provided a constant feedstock is available, the product has more constant characteristics than in batch operation. Once steady state conditions are established, the drift is only slow and can generally be adjusted by pressure control on the reactor system. The main disadvantage is that a continuous installation is inflexible. A changeover to a different feedstock or a different end product requires ca. 3 times the residence time in the system, and during this period off-standard product is obtained.

Virtually all practical continuous hydrogenation installations are cascades of a number of stirred tank reactors. If a single stirred tank is used in a continuous regime, there is a wide spread in residence times. By connecting a number of reactors in series in a cascade, the time distribution curve is narrowed. For most practical purposes, a five- or six-unit cascade is considered sufficient. Even then, however, the width of the distribution curve is not negligible. The result is

that part of the charge stays in the reactor system longer than the average residence time, while another part stays in less than the average time. The product may thus be regarded as a mixture of too much and too little hydrogenated oil, containing too much saturated and too much polyunsaturated components, respectively. A residence time distribution lowers the selectivity. Accordingly, the SCI-temperature curve is somewhat less steep for a continuously hydrogenated product than for a batch product at the same iodine value. Repeatedly, proposals have been made (11) to perform continuous hydrogenation in a packed bed column containing catalyst pellets, through which oil and hydrogen are passed concurrently or in countercurrent. From our earlier discussion, it is obvious that with macroscopic catalyst pellets the conditions for pore transport of triglycerides to become rate-limiting are pushed to the extreme: due to the compression applied in pelletizing, pores are certainly not wider than in the starting material. In operation, utilization of the catalyst will be very poor, since the core of the pellets will be completely filled with tristearate. Only the outer shell of the pellets contributes to the hydrogenation, but selectivity is extremely poor.

End Point Control

In batch operation, the method of end point control most generally applied consists of drawing samples at short intervals when the desired end point is approached and measuring the slip point or refractive index. For a given oil, the latter is almost linearly related to the iodine value. Optionally, the reaction is retarded near the end point by switching the stirrer to a slower speed or by limiting the hydrogen supply.

Although in this way a reasonable measure of success is achieved, it cannot be denied that the SCI-values for successive batches show a considerable spread. Most of the deviation is due to deviation in the iodine value of the product. It would therefore be highly desirable if the iodine value or some related quantity could be continuously monitored and recorded on a strip chart.

Commercial apparatus is available for continuous refractometry, densitometry, and infrared spectroscopy. The latter apparatus continuously records content of *trans*-acids. A common problem with these installations is that the presence of catalyst in the sample stream tends to cause fouling, drift, and blockage of the system, so that frequent accuracy checks and maintenance are needed. Moreover, the investment for the complete explosion-proof system is considerable, and the system hardly lends itself for use on more than one hydrogenator.

Another principle is based on metering the hydrogen consumption by the vessel. Accurate instruments for measuring hydrogen mass flow both in and out are available. Gland leakage on the stirrer shaft should be nil, and, with modern seals and proper maintenance, this can be achieved. The system can be used only in conjunction with a weighing tank for the charge. This system works reliably in practice. In continuous hydrogenation, the control problem is simpler. Provided the system is well designed and is fed from a relatively large storage tank of neutralized bleached oil, and provided the catalyst has constant characteristics, the drift in end point characteristics will be very small and in any case slow. Periodic sampling and conventional analysis will then indicate whether marginal adjustments are needed. If so, these can be effected by adjustment of the catalyst proportioning pumps, changing the ratio of fresh and recirculated catalyst, or by pressure adjustment. Obviously, some experience in the response of the system to these adjustments is required.

WHAT REMAINS TO BE DESIRED—CATALYSTS OTHER THAN NICKEL
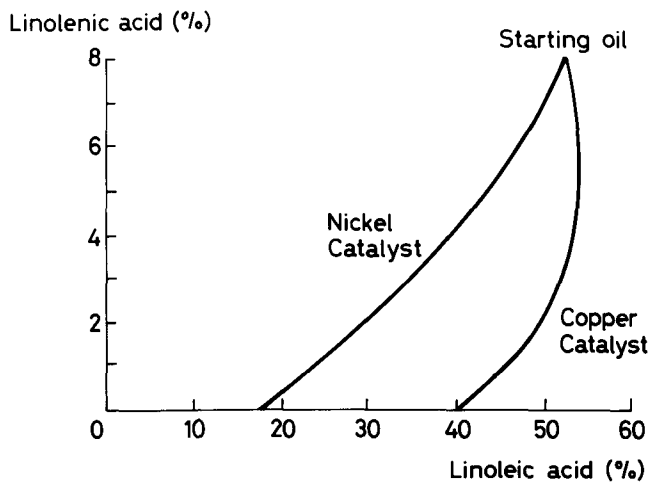
Hydrogenation with nickel catalysts is extremely

FIG. 14. Linolenic acid content as a function of the linoleic acid content in soybean oil hydrogenated at 185 C with nickel and copper catalysts.

FIG. 15. Comparison of hydrogenation of soybean oil with four catalysts: 1 = (Arene)Cr(CO)$_3$, 180 C, 30 atm; 2 = Cu, 180 C, 5 atm; 3 = Ni, 100 C, 3 atm; 4 = Ni(S), 180 C, 1 atm. IV = iodine value.

versatile. By choice of conditions, the selectivity can be controlled within certain limits and the end point at which hydrogenation is stopped can also be chosen. As a result, a virtually infinite number of different hydrogenated products can be made from any simple starting oil. Nonetheless, hydrogenation with nickel has well defined limitations:

1. Selectivity I is never absolute, unless extreme conditions are used, with the danger of side reactions.
2. Nickel catalysts have little preference for linolenic acid over linoleic acid, so that a considerable sacrifice in linoleic acid has to be made if linolenic acid is to be eliminated from, for instance, soybean oil for stability reasons. In the process, important amounts of trans-acids are also formed, so that the liquid character of the oil is lost.
3. Selectivity and isomerization are coupled. It is impossible to hydrogenate selectively with low trans-acid formation, a serious drawback in the preparation of stable liquid frying oils.

Nickel catalysts, in repeated use, accumulate catalyst poisons which not only lower the activity but also affect the selectivity, postively or negatively, depending on the type of catalyst poison. Sulphur generally increases S_I, S_T, and S_i, resulting in high levels of trans-acids and very steep SCI-temperature curves. The effect is most pronounced for a nickel catalyst intentionally poisoned with sulphur.

Copper catalysts have been found to have an absolute selectivity I (12), so that lower melting or more liquid products are obtained than with nickel catalysts at the same iodine value. Moreover, copper catalysts have a much higher preference for linolenic acid (13-17), so that in elimination of this acid from soybean oil, much less linoleic acid is sacrificed. The effect is illustrated in Figure 14 (17).

With copper catalysts, it is possible to hydrogenate soybean oil to a product still liquid at room temperature and having < 1% linolenic acid content. A serious drawback of copper catalysts is that they are much less active than nickel catalysts and much more sensitive to poisoning, which lowers the selectivity. Therefore, reuse is hardly possible and overall consumption is 5-10 times higher than that of nickel catalysts. A special posttreatment is needed to eliminate the last traces of copper because of its prooxidant effect. The fat in the filter cake degrades very fast on exposure to air, another loss factor unless special measures are taken. For these reasons, application of copper hydrogenation remains limited. Recently, similar selectivity advantages, without some of the drawbacks, have been claimed for nickel-silver catalysts (18,19).
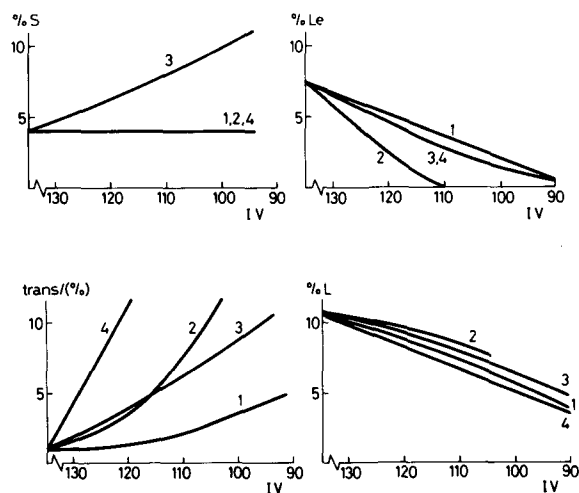
In recent years, novel types of hydrogenation catalyst have been found. These are soluble coordination complexes of transition metals which act as homogeneous catalysts. Although many of these have high activity and reasonable selectivity, their performance is not sufficiently unique to warrant their application. A complex which combines practically absolute selectivity I with very low trans-acid formation is an arene chromium carbonyl complex (20-22). In Figure 15, the course of the fatty acid contents is compared for hydrogenation with the chromium complex, copper catalyst, nickel catalyst, and sulphided nickel catalyst. For the nickel catalyst, conditions were chosen to minimize trans-acid formation, resulting in considerable loss in selectivity I. The chromium complex catalyst is a highly interesting development but as yet not ripe for practical application due to low activity, high cost, and difficult handling.

REFERENCES

1. Unilever Ltd., Economics and Statistics Department, World Oils and Fats Statistics 1971-74, June 1975.
2. USDA, Fats and Oils: FFO 5-73, March 1973.
3. USDA, Fats and Oils: FOP 7-75, July 1975.
4. Coenen, J.W.E., "The Contribution of Chemistry to Food Supplies," IPUAC Symposium, Hamburg, West Germany, 1973; Butterworths, London, England, 1974.
5. Coenen, J.W.E., J. Oil Technol. Assoc. India 16 (1969).
6. Coenen, J.W.E., and H. Boerma, Fette Seifen Anstrichm. 70:8 (1968).
7. Heertje, L., and H. Boerma, J. Catal. 21:20 (1971).
8. Coenen, J.W.E., H. Boerma, B.G. Linsen, and B. de Vries, Proc. 3rd Int. Congr. Catal., Amsterdam, The Netherlands, 2:1387 (1964).
9. Keppen, J.G., M.M. Horikx, P.W. Meyboom, and W.H. Feenstra, JAOCS 44:543 (1967).
10. Coenen, J.W.E., Th. Wieske, R.S. Cross, and H. Rinke, Ibid. 44:344 (1967).
11. Mukherjee, K.D., J. Kiewitt, and M. Kiewitt, Ibid. 52:282 (1975).
12. Hilditch, T.P., and C.W. Moore, J. Soc. Chem. Ind. London 1923:15 T.
13. Unilever N.V., Dutch Pat. Appl. 295,863 (1963).
14. de Jonge, A., J.W.E. Coenen, and C. Okkerse, Nature 206:573 (1965).
15. Koritala, S., and H.J. Dutton, JAOCS 42:144A (1965).
16. K.K. Nikki Kagaku: U.S. Pat. 3,169,981 (1965).
17. Okkerse, C., A. de Jonge, J.W.E. Coenen, and A. Rozendaal, JAOCS 44:152 (1966).
18. Lefebvre, J., and J. Baltes, Fette Seifen Anstrichm. 77:125 (1975).
19. German Pat. Appl. 2,246,830 (1974).
20. Frankel, E.N., and F.L. Little, JAOCS 46:256 (1969).
21. Frankel, E.N., and F.L. Little, Ibid. 47:11 (1970).
22. Frankel, E.N., and F.L. Little, Ibid. 47:497 (1970).