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Influence of Various Catalyst Poisons and Other Impurities on Fatty Acid Hydrogenation

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ABSTRACT

The effect of various impurities which reduce the activity of nickel catalysts during fatty acid hydrogenation has been studied. It is here proposed to divide the compounds which negatively influence the nickel-based fatty acid hydrogenation process into three categories, namely, catalyst poisons, inhibitors and deactivators, each group acting according to a different mechanism. The deleterious effect of typical catalyst poisons, such as S, N, P or Cl, is more or less independent of the chemical nature of the individual organic compounds containing these elements. There is good correlation between these element contents and the required nickel catalyst loading level. Other typical impurities present in technical fatty acids, such as oxidized fatty acids, soaps and water, also diminish the catalyst activity considerably. A number of experiments were designed to study the influence of various pretreatments of fatty acids on the catalyst loading levels needed for hydrogenation. In view of the high cost of nickel catalysts, considerable savings can be obtained by pretreatment of fatty acids prior to hydrogenation. Such pretreatment steps may include sulfuric acid washing, application of spent catalysts, and/or distillation. The most economical method will depend on local circumstances.

INTRODUCTION

The influence of catalyst poisons during hydrogenation of oils and fats in the presence of nickel catalysts has been studied in several investigations (1-6). Generally, all impurities reducing the catalyst activity have been termed "catalyst poisons," independent of their chemical nature or their origin. These impurities are either typical constituents of natural oils and fats or decomposition products or may be introduced during processing. These undesired compounds are not completely removed during oil refining and only to a small extent in the splitting process, which is normally the first step during fatty acid manufacture.

The fatty acid industry has an additional handicap because its raw materials are, in most cases, byproducts (acid oils) of edible oil refining or nonedible oils and fats, containing large quantities of impurities which adversely affect the hydrogenation of fatty acids. A split tallow fatty acid, for example, may contain the following catalyst poisons (in mg/kg): sulfur, 5-25; phosphorus, 10-50; chlorine, 10-100; and nitrogen, 200-600. Since industrial hydrogenation of fatty acids has to be as fast and as economical as possible, it is evident that impurities inhibiting the hydrogenation process play a very important role. Typical recommendations for the catalyst loading level in industrial hydrogenation of fatty acids of different quality are illustrated in Figure 1. This shows that, compared to edible oil hardening, large quantities of nickel catalyst are needed in fatty acid hydrogenation.

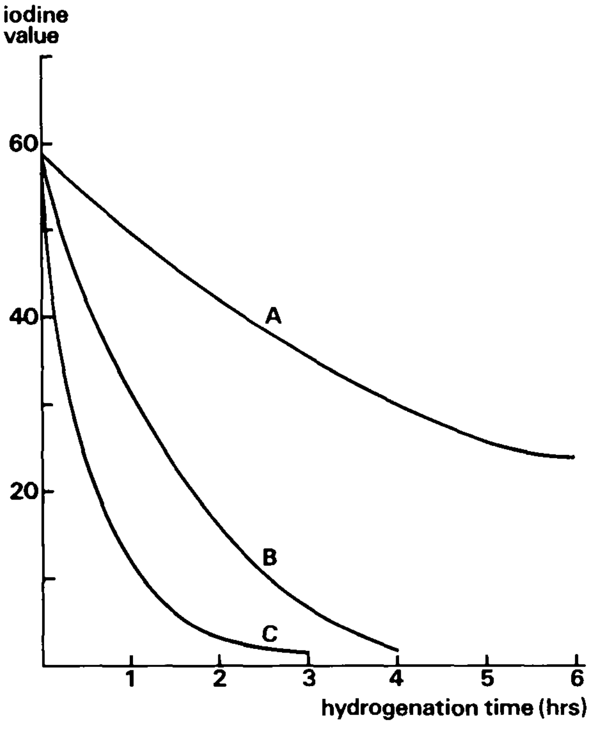

FIG. 1. Recommended catalyst loading levels in fatty acid hydrogenation. (A) Split fatty acid, 0.06% wt Ni; (B) split fatty acid, 0.24% wt Ni; (C) distilled fatty acid, 0.06% wt Ni.

The objective of the recent study was to determine in a quantitative way the influence of catalyst poisons and other impurities in fatty acids during hydrogenation in the presence of supported nickel catalysts and to suggest ways and means to overcome the excessive nickel catalyst use.

EXPERIMENTAL PROCEDURES

Materials

To obtain a control sample for the hydrogenation trials, a fatty acid of very high purity was required. Therefore, a refined and bleached tallow was used as a starting material for the preparation of a double distilled fatty acid. The tallow fatty acid prepared in such a way was practically free of catalyst poisons (S = 0 ppm; Cl = 0 ppm; P = 1 ppm; N = 6 ppm). The water content was 0.01%, the peroxide value was zero and the iodine value (IV) was 52.6.

To measure the influence of various catalyst poisons in a quantitative way, model fatty acids have been prepared by adding to the "poison-free" fatty acid (control) the following compounds: 5-sulfosalicylic acid (5, 10, 25, 50 mg S/kg fatty acid); hexachlorocyclohexane or aldrin (3, 5, 10, 50 mg Cl/kg fatty acid); lecithin (10, 50, 100 mg P/kg fatty acid), and l-leucine or choline (50, 100, 300 mg N/kg fatty acid).

To crosscheck the correlations found between the content of catalyst poison and catalyst loading level, a split tallow fatty acid of poor quality has also been tested. It contained 21 ppm S, 32 ppm P, 80 ppm Cl and 510 ppm N.

In addition, the effect of various contaminants in fatty acids on catalyst consumption has been examined, e.g., the influence of 0.2-0.5% sodium soaps or 0.5-2.5% oxidized fatty acid in tallow and soy fatty acids.

Most of the experiments used a Unichema PRICAT 9912 sample, having 22% nickel and a nickel surface area of 120 m^2/g Ni. Some experiments with other commercial catalysts have also been done under comparable conditions. The hydrogen used in all of the tests had a purity of 99.9%.

Hydrogenation

Hydrogenation tests were made in a 500-mL autoclave. The following hydrogenation conditions were kept constant: temperature = 200 C; pressure = 30 bar; stirring rate = 850 rpm; hydrogenation time = 150 min; fatty acid sample weight = 300 g. The catalyst loading level (0.01% Ni) of the control run with pure distilled tallow fatty acid was determined in such a way that under the above conditions an iodine value of one was obtained after hydrogenation.

The fatty acid and the catalyst were charged into the reactor, degassed, and heated under nitrogen to 200 C. The autoclave then was flushed with hydrogen, the pressure was adjusted at 30 bar, and stirring was started.

Samples were taken during hydrogenation and the iodine values were determined by the Wijs method. In a first series of experiments with the model fatty acids containing various accurate levels and types of catalyst poisons, the nickel loading level was also kept constant at 0.01%.

Pretreatment of Fatty Acids

The split tallow fatty acid (IV = 57.6) based on special tallow was pretreated prior to the standard hydrogenation trials. Sulfuric acid washing was done at a 1:1 ratio of a 5% sulfuric acid and fatty acid at 100 C and 30 min, followed by water washing and drying of the fatty acid. A pretreatment of the split fatty acid was also made with 0.05% and 0.1% of fresh or spent nickel catalyst at 160 C for 1 hr. Prior to the hydrogenation test, the poisoned catalyst was filtered off or left in the sample. Straight distillation of a split tallow fatty acid sample was done in a laboratory distillation unit at 180-220 C bottom temperature and at 0.2-0.3 mbar pressure.

RESULTS AND DISCUSSION

Relatively little information is available about the exact structure of the compounds which reduce the catalyst activity during hydrogenation. It is also difficult to understand fully the complex mechanisms which produce deactivation.

Based on our past and recent experimental work we have proposed dividing the impurities in fatty acids which affect the hydrogenation process (in the presence of nickel catalysts) into three categories: catalyst poisons (S, N, P, Cl, As); catalyst inhibitors (decomposition products, gums, alkali soaps, oxidized fatty acids); and catalyst deactivators (acids, water, carbon monoxide). The action of the impurities of these three groups is not straightforward and a certain overlapping of the effects is apparent.

Among the impurities influencing fatty acid hydrogenation, the so-called "catalyst poisons" are the most prominent. Effective poisons for nickel catalysts are generally found in compounds containing elements of the groups V, VI and VII of the Periodic Chart of Elements which possess lone electron pairs, e.g., sulfur or phosphorus. The interaction is being accomplished by electron donation to the unoccupied d-orbitals of the catalyst metal.

In this study, all substances which are able to cause catalysts to become irreversibly inactive according to such a mechanism are termed "catalyst poisons." It is assumed that these poisons are concentrated at the surface of the catalyst. In the case of sulfur, another mechanism has been reported (7) whereby, because of interaction between hydrogen and sulfur-containing compounds at the nickel catalyst surface, sulfur is released, which reacts with the nickel, thereby reducing the nickel surface area and consequently lowering the catalyst activity. At our laboratories, spent nickel catalyst samples have been analyzed and it was found that they contain, e.g., 0.5-2.5% sulfur or 0.5-2.0% phosphorus.

During practical hydrogenation we have to differentiate between gaseous poisons stemming from the hydrogen and a variety of poisons which are present in the oils, fats and/or fatty acids. Sulfur-containing compounds, such as hydrogen sulfide, carbon disulfide and sulfur dioxide, are the most prominent gaseous poisons. It is known that they deactivate a catalyst according to the sulfur content and are practically independent of the type of compounds.

For the hydrogenation experiments, catalyst poisons containing organic substances with a relatively low molecular weight have been chosen to eliminate both the possibility of steric hindrance and the effect of certain larger molecules, such as phosphatides, which can be adsorbed at the pore entrance of the catalyst, as described by Ottensen (8). Furthermore, it has to be assumed that, especially for fatty acids, as a result of process history degradation products will play a bigger role. Compounds, such as choline and ethanolamine, stemming from phospholipids have been analyzed in fatty acids.

As a result of the recent laboratory hydrogenation trials with fatty acids containing various defined amounts of catalyst poisons, it can be concluded that they have a similar destructive effect, as described in previous publications dealing with hydrogenation of neutral oils and fats (1-6). The reduction of the catalyst activity caused by the elements S, P, Cl and N is demonstrated in the diminished reaction rates as shown in Figures 2-5.

The effect of the various catalyst poisons on reaction rates in fatty acid hydrogenation can also be illustrated by the "relative hydrogenation efficiency" (rHE), which has

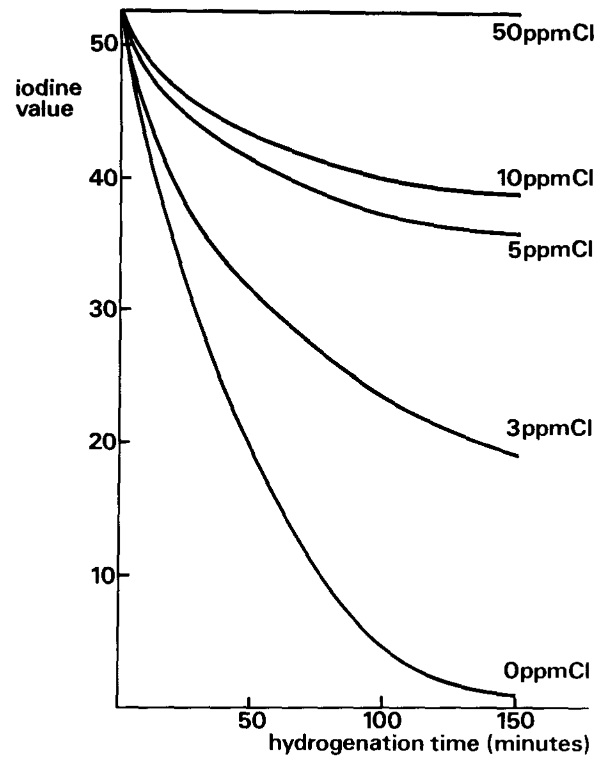

FIG. 2. Effect of chlorine on reaction rate.

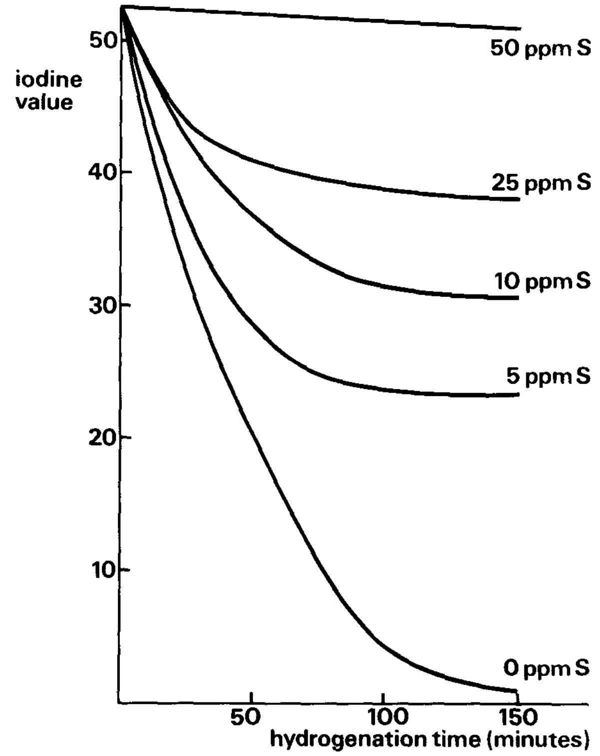

FIG. 3. Effect of sulfur on reaction rate.

been defined as

$$rHe = [(IVo - IVp) / (IVo - IVc)] \times 100\%$$

whereby IVo = iodine value of the pure tallow fatty acid (control), IVc = iodine value of the control after hydrogenation, and IVp = iodine value of the poisoned tallow fatty acid after hydrogenation.

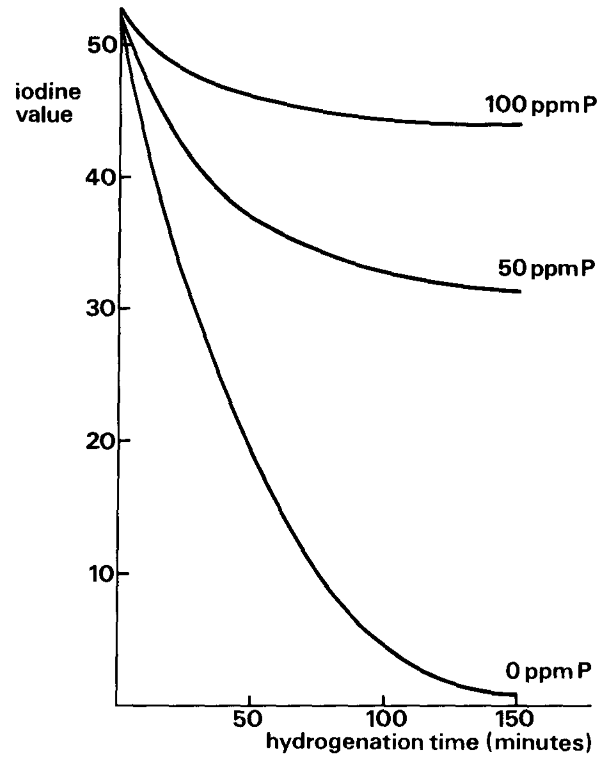

FIG. 4. Effect of phosphorus on reaction rate.

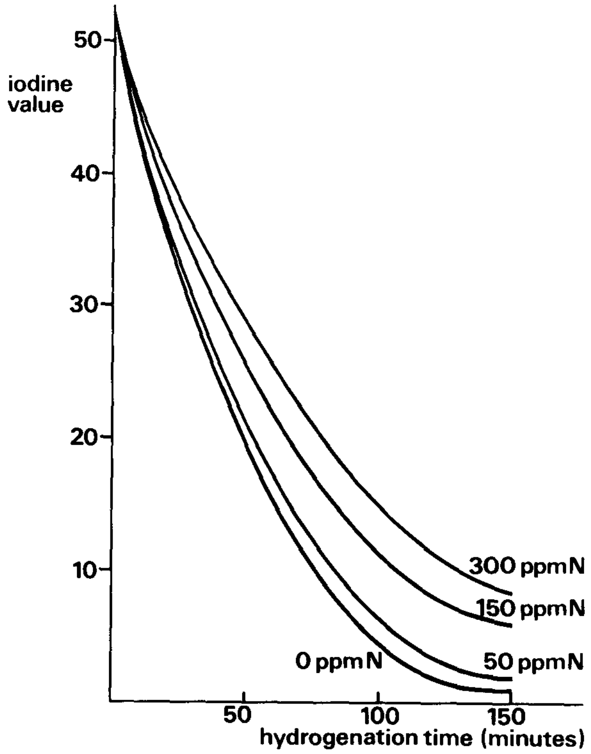

FIG. 5. Effect of nitrogen on reaction rate.

Results of these calculations are summarized in Figure 6, which shows that chlorine has the most deleterious effect on fatty acid hydrogenation, followed by sulfur. The effect of phosphorus-containing compounds is moderate, and rather low for nitrogen-containing compounds.

In a second series of experiments, the catalyst input for hydrogenation of the poisoned (model) fatty acids was increased to such a level that iodine value drops similar to the

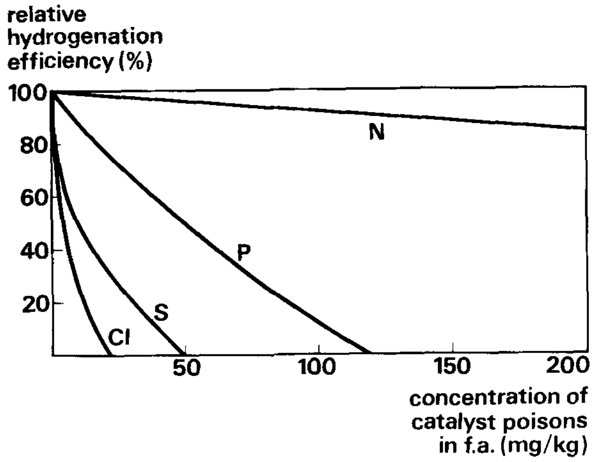

FIG. 6. Influence of catalyst poisons on relative hydrogenation efficiency.

control run were obtained. In this way, accurate figures for the additional catalyst quantities, offsetting the poison effect, were obtained. The following correlations were established: 1 ppm chlorine, sulfur, phosphorus and nitrogen, respectively, poisons 0.003%, 0.002%, 0.0006% and 0.0002% nickel, respectively. These nickel consumption figures are somewhat lower than those given by Ottensen (2), who tested the effect of catalyst poisons in neutral oil hardening. As opposed to neutral oil hardening, nitrogen-containing compounds have little effect on fatty acid hydrogenation. It has, however, to be considered that Ottensen used a catalyst with a nickel surface area of only 70 m^2/g Ni.

According to Coenen and Linsen (9), at the surface of a catalyst, two nickel atoms are poisoned by one sulfur atom. Consequently, 1 mg sulfur would poison a nickel surface area of 2.38 m^2. Using these correlations, the figures found for sulfur in the practical trials show good agreement.

To check the validity of the established nickel consumption figures of the various catalyst poisons in a practical case, tallow fatty acid of poor quality has been hydrogenated under standard conditions using various catalyst loading levels. The tallow fatty acid contained 510 ppm N, 32 ppm P, 21 ppm S and 80 ppm Cl, respectively. The target iodine value has been obtained with a catalyst input of 0.450% Ni. This figure corresponds very well with the calculated nickel amount of 0.403%.

A few experiments were also made with other commercially available supported nickel catalysts. Generally speaking, it can be stated that all nickel catalysts are affected by catalyst poisons and that any differences in poison resistance are caused by variations in quality, e.g., different nickel surface areas.

Besides catalyst poison containing elements, such as S, N, P, Cl or As, which are strongly attached to the Ni surface via electron donation, there is a second group, which we have termed "catalyst inhibitors." These are impurities, such as decomposition products, gums, oxidized fatty acids or alkali soaps, which will be adsorbed, e.g., at the entrance of the pores of the catalyst surface. The inhibiting effect on hydrogenation is simply caused by physical blocking of active centers of the catalyst.

The effect of contamination of tallow and/or soy fatty acid with 0.2% and 0.5% sodium soaps or 0.5-2.5% oxidized fatty acids was tested in standard hydrogenation trials. The influence of these impurities, however, is not as pronounced as for catalyst poisons: viz. 0.1% oxidized fatty acids consumes 0.003% nickel and 0.1% sodium soap requires additional 0.002% Ni. The effect of alkali soaps and oxidized fatty acids during hydrogenation is much more evident for oils and fats than it is for fatty acids.

The third group, called "catalyst deactivators" decreases the hydrogenation reaction rate because the compounds can react chemically with the nickel crystallites. Carbon monoxide belongs to this category and certainly at temperatures below 160 C it has to be considered as a powerful catalyst deactivator.

To complete this aspect of the study, the influence of water and carboxyl groups as possible catalyst deactivators has to be discussed. Compared to edible oil and fat hardening, much higher quantities of nickel catalyst are used in hydrogenation of fatty acids. This has been primarily attributed to the presence of catalyst poisons and of free carboxyl groups. However, already at the beginning of the experiments, when the parameters for the hydrogenation of the control tallow fatty acid were established, it was found that 0.01% Ni was sufficient to lower the iodine value to the required figure of one in the "standard" hydrogenation time of 150 min. This surprising result revealed that the substantial loss in Ni catalyst activity observed in practical fatty acid hydrogenation is caused predominantly by the catalyst poisons, deactivators and inhibitors normally present in technical fatty acids, whereas free carboxyl groups obviously play only a secondary role.

The experiments have demonstrated that distilled tallow fatty acids of high quality, for example, can be fully hydrogenated applying only 0.01% Ni. Such a catalyst input has to be considered as low, even for hydrogenation of refined and bleached edible oils. From other work it is known that the geometric type of the pore structure (size and shape) of the catalyst is responsible for the accessibility. This, together with the particle geometry and the crystallite size and distribution, determines the overall activity. It becomes obvious that during hydrogenation these parameters are changed or influenced by various compounds other than fatty acids, hence resulting in decreased activity of the catalyst.

The role of water as a powerful catalyst deactivator is often underestimated in practical hydrogenation. Preferentially the small (and very active) nickel crystallites readily react with water according to the equation:

$$\mathrm{Ni} + \mathrm{H_2O} \rightleftharpoons \mathrm{NiO} + \mathrm{H_2}$$

The nickel oxide then reacts with the fatty acids:

$$\mathrm{NiO} + 2\,\mathrm{R}-\mathrm{COOH} \rightleftharpoons (\mathrm{RCOO})_2\mathrm{Ni} + \mathrm{H_2O}$$

Although nickel soaps can be reduced to metallic nickel under the conditions of fatty acid hydrogenation, Coenen and his coworkers (10) have reported that the reduction of nickel soaps in the presence of a nickel catalyst for the greater part takes place on the nickel surface of the catalyst, resulting in a nickel crystallite increase. This effect has been confirmed by measuring the nickel crystallite size before and after hydrogenation in the presence of nickel soaps (10).

Experiments to quantify the influence of water in fatty acid on catalyst consumption have shown that for a water content of up to 1%, ca. 0.008% additional Ni has to be added for every 0.1% water. It has, however, to be pointed out that the effect of water is very complex and is also very much dependent on the overall hydrogenation conditions.

The influence of various impurities which decrease the reaction rate during fatty acid hydrogenation is of paramount importance for the catalyst consumption.

Since the catalyst is by far the most costly raw material in fatty acid hydrogenation, various pretreatments of split tallow fatty acids have been investigated on laboratory scale. The results of the pretreatment/hydrogenation trials are summarized in Table I. They indicate that pretreatment of the fatty acid with spent catalyst prior to hydrogenation with fresh catalyst has some influence on catalyst consumption. Approximately 40% Ni can be saved. The results demonstrate that, at least in the case of tallow fatty acids, distillation is by far the most effective way to remove impurities adversely affecting the hydrogenation process. Under the stated conditions a split tallow fatty acid yielded an IV of 9.6, using 0.25% Ni. After a straight distillation of the split tallow fatty acid, the corresponding hydrogenation trial ended at an IV of 5.8, although only 0.0625% Ni was applied.

TABLE I

Effect of Pretreatment of Split Tallow Fatty Acid (IV = 57.6) on Hydrogenation Rates[1]

Run	Pretreatment	Final IV
1 a	No pretreatment	47.3
1 b		9.6
2 a	H_2SO_4 wash	41.3
2 b		4.5
3 a	0.1% Ni (fresh), with filtration	40.8
3 b		4.2
4 a	0.1% Ni (spent), with filtration	37.8
4 b		3.3
5 a	0.1% Ni (spent), no filtration	39.2
5 b		4.4
6 a	0.05% Ni (spent), no filtration	41.3
6 b		4.4
7 a	Straight distillation	5.8
7 b		1.0

[1] Standard hydrogenation conditions: 300 g fatty acid; 200 C; 30 bar; 850 rpm; 150 min.
Run a with 0.0625% Ni; run b with 0.25% Ni.

There are also a few other methods of pretreating fatty acids prior to hydrogenation, e.g., use of bleaching earth. The cost of such purification steps has to be calculated and compared with catalyst savings. The most economical way will depend upon local circumstances.

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Fatty Acid Fractionation by Column Distillation: Purity, Energy Consumption and Operating Conditions

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ABSTRACT

This paper discusses the optimal process conditions for production of individual fatty acids of any desired purity up to higher than 99% and describes especially the influences of column internals as well as exchange numbers, reflux ratios and fatty acid residence times at distillation temperatures. The new process conditions are characterized by degasification at low temperatures followed by efficient dehydration together with separation of first cuts at high reflux ratios by short-time dephlegmation. The design of columns for efficiency and low pressure drop is influenced by the thermal properties of crude acids and the quality demands on distillate fractions. Environmental requirements can be met by working without open steam. Bottom temperatures should not exceed 250 C, to prevent thermal degradation of fatty acids as well as corrosion of stainless steel.

FATTY ACID FRACTIONATION IN THE PAST

Industrial separation of individual fatty acids with high purity by column distillation from raw acids of natural origin such as from splitting different kinds of vegetable oils or animal fats is a fairly new technique (1-7). This process came into use mainly after World War II using bubble cap or packed columns (8-13) with unsaturated open steam (14) for lowering the evaporation temperatures to avoid thermal degradation of the heat-sensitive fatty acids (15-17). Early pioneers in this field were R. A. Potts and F. B. White (1,8,9,11-14). More recently, the economics and environmental regulations have changed decisively. Also the demands for purity have increased greatly. Therefore, new process principles became necessary which influenced equipment construction as well as operation conditions (18-26).

THE BASIS FOR A NEW FRACTIONATION PROCESS

The most important step in a new process was complete removal of open steam as part of developing new high effective column construction with very low pressure drop, together with new evaporation and condensation systems (18-25). Besides using special distillation columns of low pressure drop, today's process is characterized by effective film degasification at moderately low temperatures, followed by efficient dehydration together with separation of the odor cut as first cuts at high reflux ratios by short-time dephlegmation and a film-type pitch separation step. According to Figure 1, the precut step consists of a once-through falling film evaporator as stripping section and an enriching zone designed as dephlegmator column in the