Homogeneously Catalysed Hydrogenation of Unsaturated Fatty Acids to Unsaturated Fatty Alcohols

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Abstract

The use of copper and cadmium oxides or soaps as catalysts for the hydrogenation of unsaturated fatty acids to unsaturated fatty alcohols has been investigated. It is shown that copper soaps homogeneously activate hydrogen. When copper and cadmium oxides are used as catalysts, they react with the acid under formation of a homogeneous soap solution. A continuous reaction system for the preparation of unsaturated fatty alcohols by hydrogenation under the influence of copper and cadmium soaps is described.

Introduction

FOR THE CATALYTIC high-pressure hydrogenation of unsaturated fatty acids to unsaturated fatty alcohols many catalysts have been developed, the majority of which are described in patent literature. Most catalysts used for the preparation of unsaturated fatty acids are mixed metal oxides on a carrier, but some patents describe the use of metal soaps as catalysts. It is assumed that the soaps react with hydrogen under formation of collodial metal particles, which are generally believed to be the actual catalyst for the hydrogenation.

In the Dutch patent No. 83,397 (1956) the hydrogenation of oleic acid to oleyl alcohol under the influence of copper and cadmium soaps is described. The conversion claimed in the patent is 85–95% at a selectivity of 95%. In this patent it is also assumed that the soaps react with hydrogen to form colloidal metal particles. We have investigated this process and the results are described in this paper.

From patent literature several catalysts for the selective hydrogenation of fatty acids to fatty alcohols are known that contain Cu and/or Cd. They can be divided into three groups: a) mixed oxides; b) metals; c) metal soaps.

If the catalyst is added in the form of mixed oxides or metal soaps, the question arises, in what form is the catalyst active during the hydrogenation. The oxide can be reduced by hydrogen to metal, but it can also react with the acid to form a metal soap. The metal soap in its turn can react with hydrogen to form a metal. Only in the case of the (fairly noble) metal catalyst is the catalyst fairly well defined.

Mixed Oxides (containing Cu and/or Cd)

One of the first catalysts for the preparation of fatty alcohols from fatty acids was the CuO/Cr_2O_3 catalyst. This catalyst presented the disadvantage of promoting the hydrogenation of unsaturated fatty acids to saturated fatty alcohols. Addition of $CdCO_3$ or Cd soap to the CuO/Cr_2O_3 catalyst gives a sharp rise in selectivity towards the forming of unsaturated alcohols. The same effect is found for the CuO/guhr catalyst, which like CuO/Cr_2O_3 is not selective. Addition of CdO results again in a higher selectivity.

Metallic Catalysts (containing Cu and/or Cd)

Only a few catalysts are in the form of metals on carrier. With Cu/Cr_2O_3/active clay unsaturated fatty acids are hydrogenated to saturated fatty alcohols, while with Cd/Cr_2O_3/active clay unsaturated fatty alcohols are formed. It is possible that in this case the active-clay carrier has a strong promoting effect on Cd/Cr_2O_3, because in other cases Cd without Cu is inactive, while in the presence of Cu it only acts as a promotor for the selectivity.

Metal Soaps

Fatty alcohols can be prepared by heating the corresponding metal soaps under hydrogen. Pb and Cd soaps of unsaturated fatty acids give as reaction product unsaturated fatty alcohols, the Cu- and Sn-soaps yield saturated alcohols and mixtures of Cu- and Cd-soaps again give unsaturated fatty alcohols.

Instead of pure soaps, solutions of metal soaps in fatty acids can be used. Cu-soaps in unsaturated fatty acids yield the saturated alcohol; Cd-, Ni-, Pb- and Co-soaps in fatty acid solutions are inactive and combinations of Cu- and Cd-soap in unsaturated fatty acid render unsaturated fatty alcohols. From the fact that pure Cd-, Ni-, Pb- and Co-soaps are active and their solutions in fatty acid inactive, we may conclude that the mechanism of the reaction between pure soaps and hydrogen is different from that of the reaction between solutions of metal soaps in fatty acids and hydrogen. The catalysts referred to are summarized in Table I (for a more complete survey see ref. 24).

In considering only those cases where a catalytic hydrogenation takes place (and thus excluding the conversion of pure soaps) two important observations can be made:

1. The form in which the catalyst, added as an oxide or as a soap, is active, is not known.
2. CuO upon a carrier and Cu-soap as such are active but not selective; CuO + CdO, CuO + Cd-soap and Cu- + Cd-soap are both active and selective.

From these facts we must conclude that whether the catalyst is added as oxide or as soap, the active form under the conditions of hydrogenation is for both cases the same. Moreover, we conclude that the carrier of the catalyst is of no importance.

Batch Process

The hydrogenation of oleic acid, methyl oleate and

TABLE I
Cu/Cd Containing Catalysts for the Hydrogenation of Unsaturated Fatty Acids to Unsaturated Fatty Alcohols

Reference	Hydrogenation of	Catalyst	Temp, C	% Alcohol	% Double bonds retained
1,2	Oleic acid	CuO/Cr_2O_3	280	64	4
3,4,5	Oleic acid	CuO/guhr	280	40	31
6,7	Oleic acid	$CuO/Cr_2O_3 + CdCO_3$	280	92	97
1	Oleic acid	CuO/Cr_2O_3 + Cd-soap	280	93	80
1	Oleic acid	CuO/Cr_2O_3 + Cd-soap	340	97	50
8	Oleic acid	Cu/Cd/Zn/Cr/O	380	75	77
5,9	Oleic acid	CuO/CdO/guhr	280	78	89
10	Sperm oil	Cd/act. clay	250	99	95
10	Linseed oil	Cd/Cr_2O_3/act. clay	250	99	99
10	Coconut oil	$Cd/Cu/Cr_2O_3$/act. clay	250	99	0
11,12	Pb oleate	....	345	85	85–95
12,13	Cd oleate	....	345	90	95
13,14,15	Cu oleate	....	345	99	14
12	Cu + Cd oleate	....	345	High	High
16,17	Palmitic acid	Cu-soap	275	97.5	
18	Oleic acid	(Cu + Cd)-soap	275	85–95	95

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olive oil under the influence of Cu- and Cd-oleate has been investigated in a normal high-pressure autoclave. The solution of Cu- and Cd-soap in one of these unsaturated compounds was placed in an open glass insert in the high-pressure vessel. The autoclave was heated by gas flames, kept at the reaction temperature for some time and then cooled. Of the resulting reaction product acid value, saponification value, ester value and iodine value were determined.

Weber (19–22) has developed a general method for describing the activity of a catalyst and especially its selectivity. If the starting material consists of two different reactive substances, A and B, the course of the reaction may be represented in an *x*-*y* diagram; *x* and *y* are the retentions of A and B respectively, expressed as A/A_0 and B/B_0 (A and B represent the concentrations of A and B, respectively, A_0 and B_0 the concentrations in the starting material). The following equation describes the change in concentration of A and B as a result of one distinct reaction variable (temperature, pressure, catalyst composition):

$$y = x + \frac{x(1 - x)}{a + bx}$$

This equation, which represents a hyperbola, allows a simple representation of a complicated chemical reaction and is of practical importance for a systematic study of catalytic processes. It was found that the course of the hydrogenation of unsaturated acids under influence of Cu- and Cd-soaps can also be represented as a hyperbola.

Figure 1 shows the course of the hydrogenation of several unsaturated fatty compounds under the influence of Cu- and Cd-soaps. The reaction conditions are summarized in Table II.

From Figure 1 we see that unsaturated compounds can be hydrogenated fairly selectively up to a conversion of 80%. At higher conversions selectivity declines sharply. In comparing curves 1 and 2, we note a rise in selectivity with falling Cu/Cd ratio. From curve 3 we see that this influence is not found at a fairly low Cu/Cd ratio (for the Cu/Cd ratios 6:2 and 4:2 the same curve was found).

Curve 4 represents the hydrogenation of oleic acid under the influence of CuO/CdO on a carrier. The ratio Cu/Cd was 2:1; 50%w metal oxide was present on the carrier. The carriers used were $MgCO_3$, MgO and guhr. The MgO was heated at 450 and 600C, which strongly reduced the specific surface. For all of these catalysts, the same curve was found, indicating that the surface of the carrier has no impact on the course of the hydrogenation. The reaction product contained Cu- and Cd-soaps, indicating that the metal oxides dissolve after formation of soaps. The same effect was found for the commercial $CuO/Cr_2O_3 + CdCO_3$ catalyst. A prereduced CuO/CdO catalyst on guhr showed no selectivity (point B in Figure 1) nor did the hydrogenation under the influence of Cu soap (point A).

The reaction products of a fairly complete hydrogenation of oleic acid (conversion about 80%) under the influence of Cu- and Cd-soaps were heterogeneous. The precipitate formed was separated by centrifuging and washed with ether, and the resulting product was examinated by X-ray diffraction. It was shown to consist of the oxides of Cu and Cd and sometimes of the metals. When such a precipitate was suspended in fresh oleic acid and subjected to the hydrogenation conditions, hydrogenation occurred if the precipitate consisted of the oxides but not when the precipitate consisted entirely of the metals. This is another indication that probably the soaps form the catalyst.

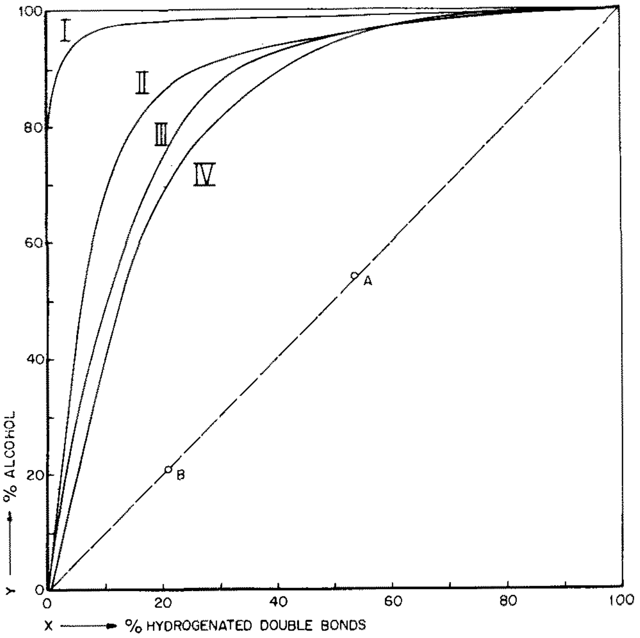


FIG. 1. Hydrogenation of unsaturated fatty acids or fats under influence of Cu- and Cd-soaps.

Summarizing, we conclude that:

1. The carrier has no influence on the hydrogenation.
2. Hydrogenation only occurs if the suspended catalyst contains the oxides.
3. The prereduced CuO/CdO/guhr catalyst is not selective.
4. The active and selective form of the catalyst is formed by the Cu- and Cd-soaps and not by the metal particles.

To get a better insight in the reaction variables of the hydrogenation of oleic acid under influence of the Cu^{2+} soap and fatty acid is heated under N_2 up to Cu- and Cd-soaps, the heating and cooling periods of the reaction vessel must be shortened drastically, because in these periods changes may take place in the reaction mixture. For instance, when a mixture of 250C, a malodorous reaction mixture is obtained, which contains Cu metal particles. Similarly, when Cu^{2+} soap in an unsaturated fatty acid is heated in the absence of H_2 polymerization may occur.

TABLE II

Reaction Conditions of the Hydrogenation of the Unsaturated Compounds Shown in Fig. 1

Curve	Hydrogenation of	Catalyst in mol %	Temp, C	Initial pressure in atm at 20C	Reaction time in min	Hyperbola const.	
						a	*b*
1	Oleic acid	Cu:Cd = 6.1:27	300	190	10–40	0.0014	1.02
2	Oleic acid	93:13	290	200	20–40	0.092	0.82
3	Methyl oleate	46:2	315	100	30	0.157	0.68
4	Oleic acid	4:2	315	120	4–80	0.148	0.83

Catalysts 1–3 are soaps dissolved in the feed.
Catalyst 4 is CuO/CdO on carrier.

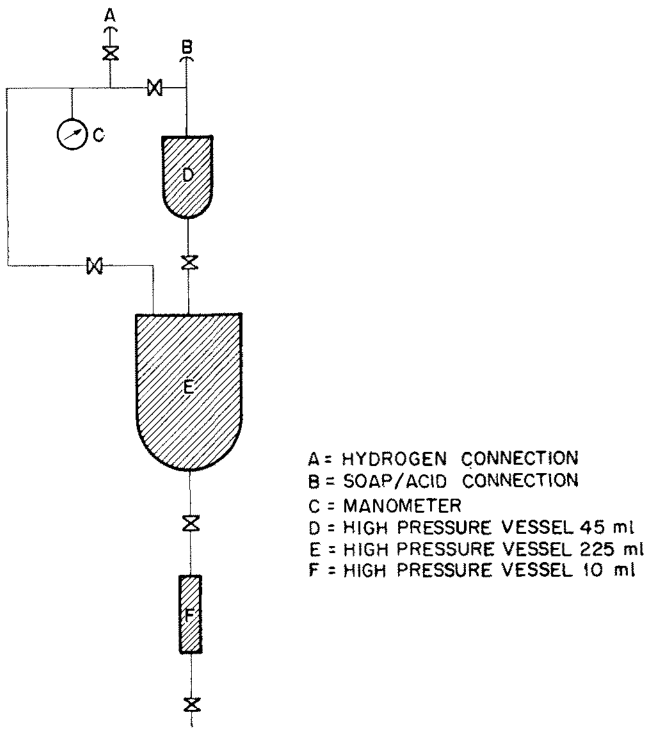


FIG. 2. Apparatus used for the hydrogenation of oleic acid.

It is further necessary to take samples in the course of the hydrogenation without stopping the reaction. A diagram of the apparatus used in our investigations is shown in Figure 2. The apparatus consists of three high-pressure vessels, connected by valves. The middle vessel E (225 ml), is filled with 100 ml hendecane solvent. This diluent is saturated with hydrogen at the reaction conditions (250C, 175 atm H_2). The upper vessel D (45 ml) is filled with 14 ml of an oleic-acid soap solution. The pressure in D is raised to 50 atm above that in E. By opening the valve between D and E, the soap acid solution is pressed into the diluent. The samples are taken from the lowest vessel F (8 ml). The whole apparatus was shaken continuously and was heated electrically; the temperature was adjusted within 1C.

The solubility of hydrogen in a mixture of 100 ml hendecane and 14 ml oleic acid was measured in the same apparatus. The results are shown in Figure 3. At the reaction conditions (250C, 175 atm H_2), about one third of the dissolved hydrogen was required for the hydrogenation. Measurements showed that the solution is saturated with hydrogen during the hydrogenation.

Results

The samples taken during the hydrogenation were homogeneous and of a dark reddish-brown colour. Cu and Cd were most probably not present in a colloidal state as no lightscattering was observed and no precipitate was obtained after 30 min centrifuging at 3000 g. The reddish-brown colour was stable under nitrogen. When the samples were exposed to air, oxidation took place and the colour changed into the blue-green colour of Cu^{2+}-soaps.

The analysis of the reaction product included the determination of saponification number, hydroxyl number and iodine number. It was found that at reaction temperatures lower than 300C no hydrocarbons were formed. From the linear change of the saponification number with time the rate of the hydrogenation was calculated. It was found that up to a conversion of 67–70% all samples were homogeneous, but beyond this figure the samples became heterogeneous and no further hydrogenation occurred. The linear change of the saponification number with time indicates that the acid concentration is not rate-determining.

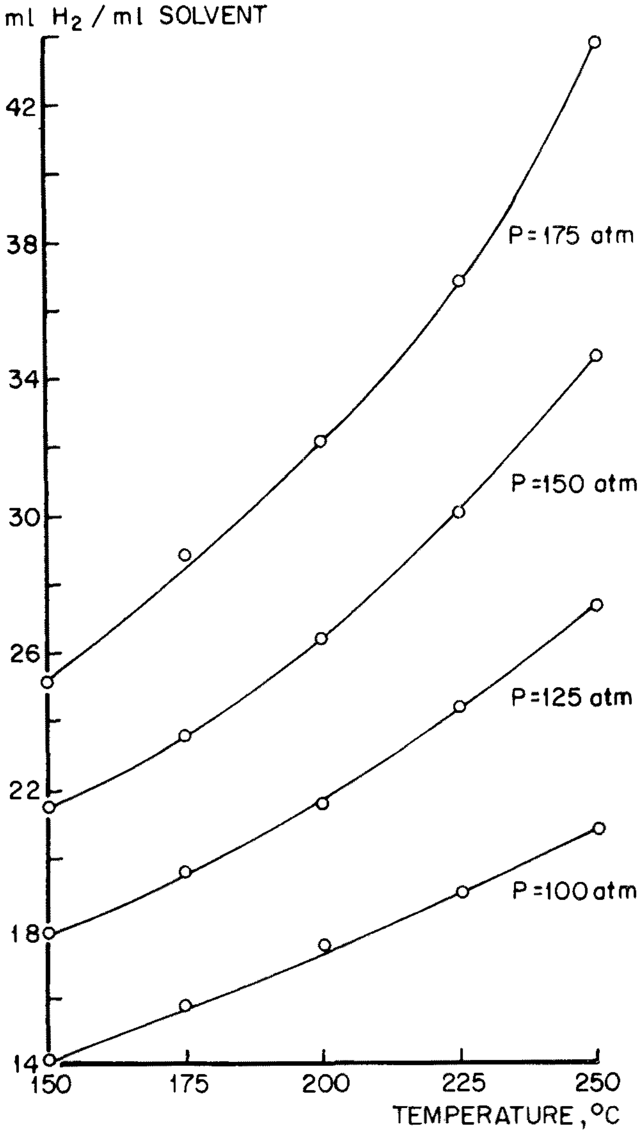


FIG. 3. Solubility of H_2 in a mixture of 14 ml oleic acid and 100 ml hendecane.

When the Cu-soap concentration was between 2.5 and 7.5% M and the Cd-soap concentration between 0.5 and 5% M (calculated on oleic acid) the hydrogenation of oleic acid was completely selective. When the Cd-soap concentration is lowered from 0.5 to 0.1% M, the selectivity progressively decreases. A remarkable fact is that the selectivity has already reached its low value in the first sample taken (after 10 min) and stays then constant. The selectivity of the hydrogenation of oleic acid under influence of 5% M Cu-soap and 0.25% M Cd-soap was 80%, with 5% M Cu-soap and 0.125% Cd-soap it was only 50%. Without Cd-soap no alcohol is formed by hydrogenation; the treated samples are heterogeneous and contain Cu metal particles.

A prerequisite for the hydrogenation of fatty acids in a metal vessel under the influence of Cu- and Cd-soaps is that the wall of the reactor must be coated with Cd or Cu-Cd. If not, the only reaction that occurs is the reduction of the soaps into the metals. After this reaction has been repeated five to ten times,

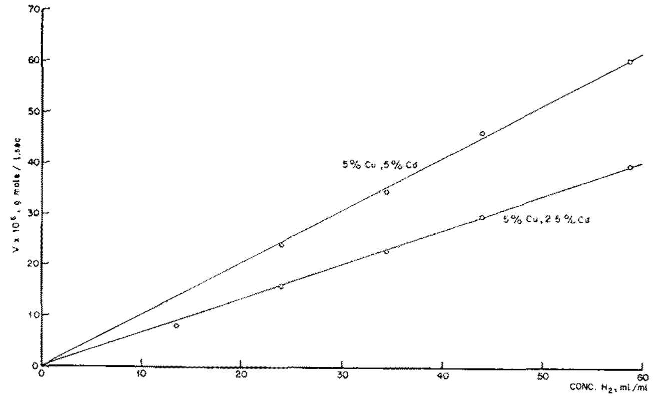


FIG. 4. Influence of the H_2 concentration on the rate of hydrogenation (T = 250C).

the wall has become coated with an adequate layer of Cu-Cd and selective hydrogenation of the fatty acids to the corresponding alcohols takes place. If the wall of the reaction vessel is of glass or Teflon, no coating with Cu-Cd is observed and the first hydrogenation is already successful.

The hydrogenation of oleic acid and linoleic acid under the influence of 5% M Cu-soap and 2.5% Cd-soap is 100% selective. During the hydrogenation of linolenic acid the iodine number falls 10% (conversion 67%). It may be that double bonds are hydrogenated, but it is also possible that a too low value of the iodine number is found owing to conjugation of double bonds.

The hydrogenation of stearic acid, myristic acid and capric acid follows the same pattern as the unsaturated acids. The relative values of the rates of hydrogenation of the various acids are:

Oleic acid	1.00	Stearic acid	1.00
Linoleic acid	0.98	Myristic acid	0.92
Linolenic acid	0.98	Capric acid	0.86

The influence of hydrogen concentration, Cu concentration, Cd concentration and temperature on the hydrogenation of oleic acid is shown in Figures 4 to 7. The influence of Cu concentration on the rate of the hydrogenation has been investigated in the presence of 2.5% M Cd-soap and without Cd-soap as well. The hydrogenations without Cd-soaps were performed after those with Cd-soap. Under these conditions about five hydrogenations can be carried out without addition of Cd-soap, but then further hydrogenations become impossible. It is assumed that a small amount of Cd from the wall of the reactor goes into solution in the experiments without Cd-soap supply, but after some hydrogenations this source of Cd is exhausted. The selectivities of the hydrogenations with 2.5, 5 and 7.5% M Cu-soap and without Cd-soap were 70, 65 and 26%, respectively, indicating that less than 0.2% M Cd-soap was in solution.

From Figures 4–7 the following rate equation is derived:

$$v = k\,[H_2]\,[Cu]\,\{1 + K\,[Cd]\,\}$$

The activation energy, calculated from Figure 7 is 26.7 kcal/mole; and appears to be independent of the Cd concentration.

The influence of the other metal soaps (Na, Zn, Mg, Ca, Ba) on the rate of the hydrogenation of oleic acid was also investigated. It was found that these soaps cannot replace the Cd-soap. The combination Cu-soap plus one of the mentioned soaps yielded no alcohol and the products were heterogeneous. These combinations were even inactive when a Teflon or glass reactor was used, indicating that a certain concentration of Cd-soap *in solution* is required for homogeneous hydrogenation. The combination of Cu with Cd and one of the mentioned soaps was active and selective. In Figure 8 the influence of these soaps on the rate of the hydrogenation of oleic acid is shown. The rate is calculated relative to the rate found with 5% M Cu-soap and 1% M Cd-soap.

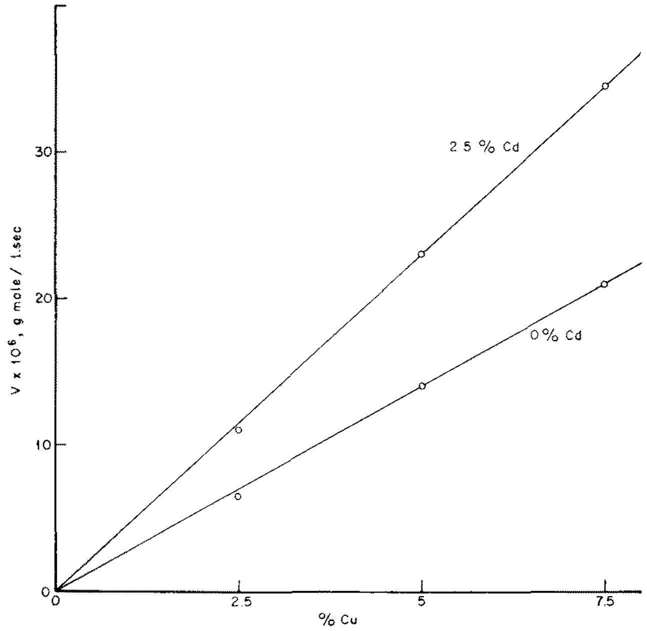


FIG. 5. Influence of the Cu concentration on the rate of hydrogenation (T = 250C, P = 175 atm).

Continuous Process

For the same reason as cited for the batch process, unwanted reactions during the heating and cooling period must be avoided in the continuous process. In consequence the feed must not be preheated in absence of hydrogen and the reaction product must be cooled quickly after leaving the reactor.

A simplified flowsheet of the pilot plant applied is shown in Figure 9. The whole apparatus was made of stainless steel 316. The reaction vessel (a stirred tank reactor) has a total vol of 500 ml, with an overflow tube placed such that the liquid vol was 300 ml. The solution of Cu- and Cd-soap in unsaturated fatty acid or unsaturated fat (without a diluent) is pumped to the reactor through a tube with an inner diameter of 3 mm. The reactants are hardly preheated before entering the reactor since high lineair velocities are realized in the narrow inlet tube. In order to reduce preheating of the feed in the inlet tube even further, the circulating hydrogen (3 liters/hr at 20C and working pressure) is fed to the reactor through the same pipe. To stop all further reactions, the reaction product leaving the reactor by the overflow tube, is immediately cooled to 75C. In order to establish high velocities in the overflow and in the product cooler, the circulating hydrogen leaves the reactor through the same overflow. The major part of the hydrogen is separated from the liquid in a high-pressure separator. The dissolved hydrogen is released from the liquid product in a low-pressure separator.

When a stirred tank reactor is used, the mean residence time required for a conversion of 80% is about 2.5 times the reaction time in a batch reactor at the same conditions. This difference is caused by the great spread in residence time in a single stirred tank reactor. It is clear that his spread influences the selec-

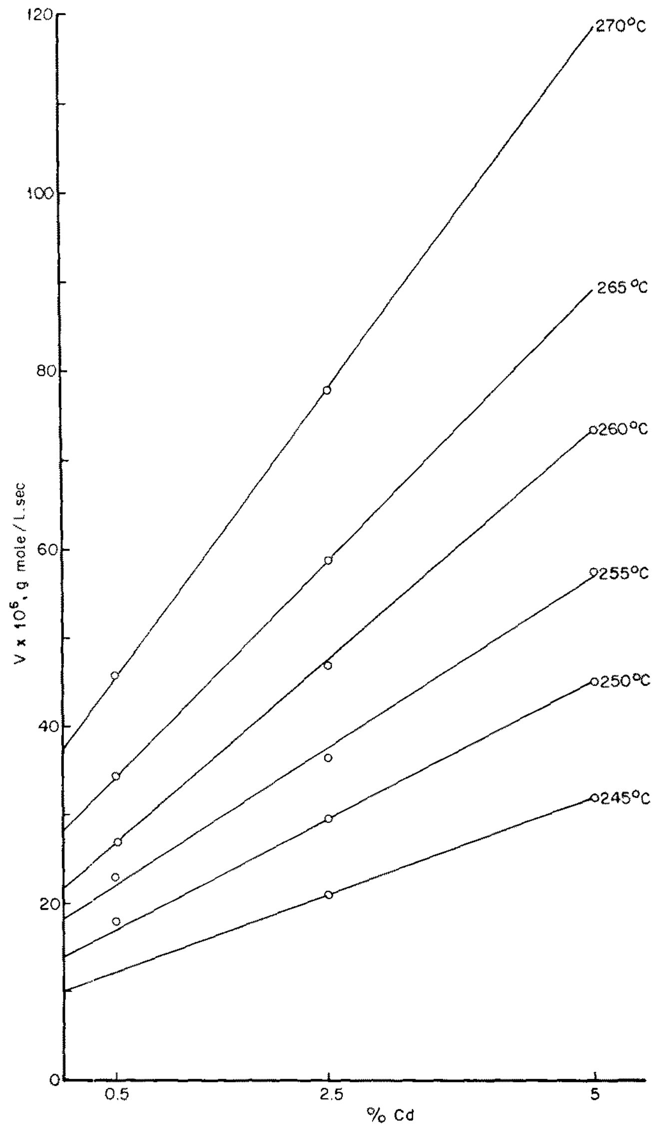


FIG. 6. Influence of the Cd concentration on the rate of hydrogenation.

tivity of the hydrogenation unfavourably. The remedy is the use of a series of stirred tank reactors or the combination of a stirred tank reactor followed by a pistonflow type tubular reactor.

With the apparatus described, the continuous hydrogenation of several saturated and unsaturated fatty acids and oils has been studied. The results are summarized in Table III.

With an improved reactor system, as mentioned, the selectivity would have been better at higher conversions. Data from the bath-process investigation indicate that conversions of 90–95% can be reached without any drop in selectivity. At higher conversions the reaction mixture becomes heterogeneous and the selectivity falls sharply. When fatty oils are used as feed for the hydrogenation, the glycerol is partly hydrogenated to propanediol. It will therefore be more economical to start from the fatty acids instead of the fatty oils.

The influence of Pb-soaps on the catalytic activity of Cu- and Cd-soaps has also been investigated in the continuous process. The reaction conditions were: 5% M Cu-soap, 2.5% M Cd-soap, 275 atm H_2, 260C and a feed rate of 120 ml oleic acid per hour. With Pb-soap concentrations of 0, 0.001 and 0.01% M, conversions of 85, 81 and 79%, respectively, were found at a selectivity of 99%. If 0.1% M Pb-soap was added, a precipitate was formed and no hydrogenation occurred.

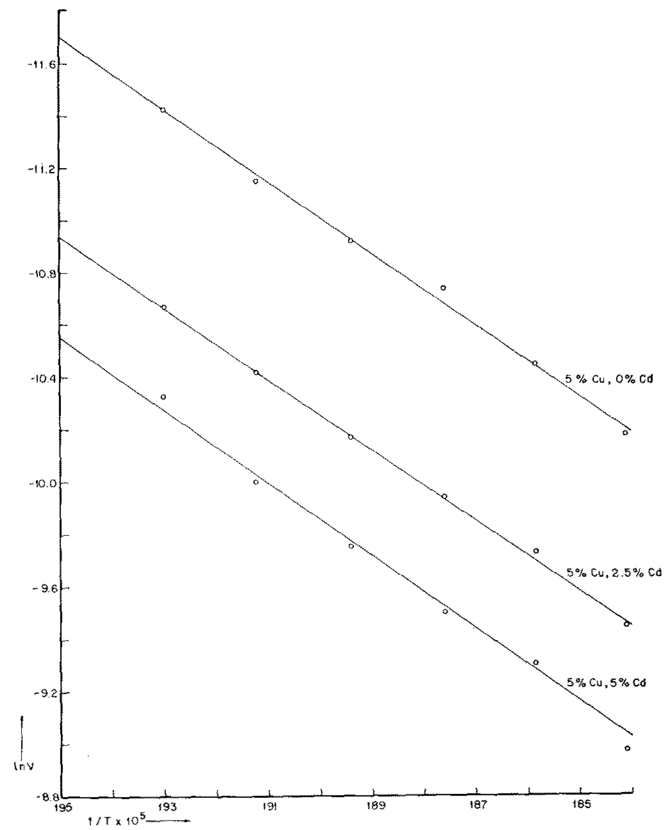


FIG. 7. Arrhenius plot for the hydrogenation of oleic acid under influence of Cu- and Cd-soaps.

Hydrogenation of fatty acids under the influence of Cu- and Cd-soaps, carried out under a partial pressure of 50 atm CO and 200 atm H_2 gave the same results as hydrogenation under a partial pressure of 200 atm H_2 without CO. In consequence cheaper CO-containing hydrogen can be used for the hydrogenation.

Reaction Mechanism

From the behaviour of the reaction product, which will be described below, it is concluded with a high degree of certainty that CuH, present as a complex with the carboxylic group and in equilibrium with the copper soap, forms the active catalyst. Although it is extremely difficult to prove that the catalyst is really molecularly dispersed, an attempt will be made to make our hypothesis acceptable.

The samples taken during the hydrogenation are very dark reddish-brown. If the hydrogenation is carried out without diluent, the cooled samples are heterogeneous because of the low solubility of Cd^{2+}- and Cu^{1+}-soaps. If hendecane, benzene or ether is added to the heterogeneous sample, a homogeneous solution is obtained. These solutions are stable under N_2 if they are exposed to an oxidizing agent like air or a Cu^{2+}-solution, the reddish-brown colour disappears and a clear colourless solution is obtained. The sensitivity of the reddish-brown solution to air makes the analysis of the solute extremely difficult (exclusion of air and deaeration of all solvents used for the analysis are required).

The compound responsible for the dark colour can be precipitated with 96% ethyl alcohol. The precipitate can be separated by centrifuging. The clear liquid

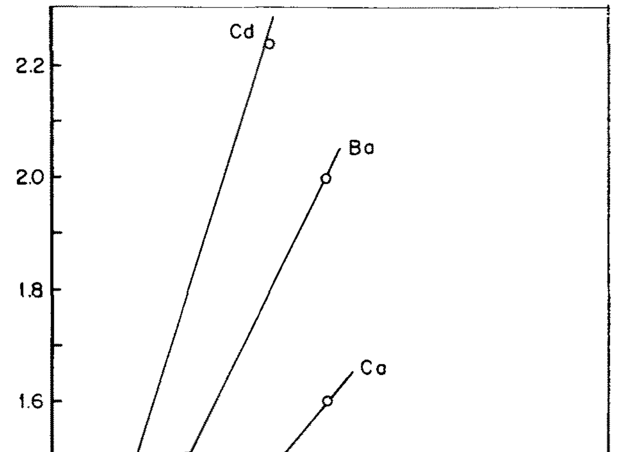


FIG. 8. Influence of metal soaps on the hydrogenation of oleic acid.

contains oleic acid, ethyl alcohol and Cd-oleate and no Cu-compounds. The precipitate contains organic matter and Cu. The amount of organic compounds (Cu^{1+}-soap, oleic acid and Cd-oleate) can be reduced by dissolution in benzene and subsequent precipitation by ethyl alcohol. The disadvantage of this procedure is that all solvents must be from oxygen, as otherwise oxidation occurs.

When the hard, brown precipitate is heated under N_2 at 200–255C, hydrogen is developed. When it is heated at 100C in the presence of benzoyl chloride, the formation of small amounts of benzaldehyde can be demonstrated with fuchsine reagent after saponification of the excess benzoyl chloride.

The red-brown solution reacts with Cu^{2+}-soap solutions and with iodine solutions. The number of hydrogen molecules developed on heating of the precipitate is about one fourth (1:3.8) of the number of Cu^{2+}-ions or iodine atoms taken up by the precipitate.

The above-mentioned reactions can be explained by the assumption that the dark colour is caused by copper hydride, CuH.

$$2\,CuH \longrightarrow 2\,Cu + H_2$$
$$CuH + J_2 \longrightarrow CuJ + HJ$$
$$CuH + 2\,Cu^{2+} \longrightarrow 3\,Cu^{1+} + H^+$$
$$C_6H_5COCl + CuH \longrightarrow C_6H_5CHO + CuCl$$

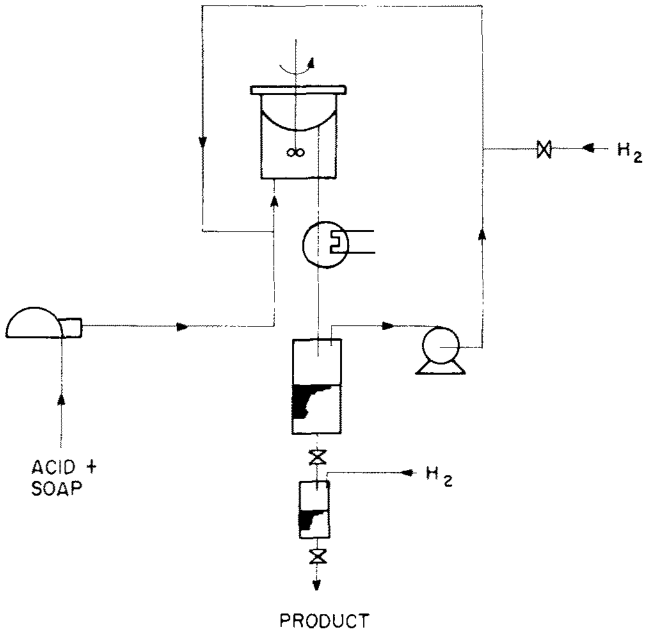


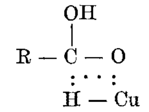
FIG. 9. Flow sheet of the continuous hydrogenation of unsaturated fatty acids or fats.

From literature (25) it is known that the solution of CuH in pyridine has a dark reddish-brown colour.

From the first order dependence of the reaction rate on the H_2 and Cu concentrations it can be concluded that the ratio of CuH to total copper is small. The value of this ratio cannot be determined because it will change during sampling (temperature and pressure change). Halpern (23) has shown, that $CuHp_2$ solutions (Hp = heptanoic acid) are reduced to CuHp by hydrogen. The hydrogenation is homogeneously catalysed by $CuHp_2$ and CuHp. The rate determining step in this hydrogenation is the reaction: $CuHp + H_2 \longrightarrow CuH + HHp$. The activation energy of this reaction is 21.0 kcal/mole (125–155C). From the fact, that the acidities of heptanoic acid and oleic acid are nearly the same, it may be expected on theoretical grounds that the activation energy of the reaction $CuOl + H_2 \longrightarrow CuH + HOl$ (HOl = oleic acid) will also be close to 21.0 kcal/mole. The experimental rate of the reduction of $CuOl_2$ to CuOl in oleic acid is in accordance with this expectation.

As stated before, the activation energy of the hydrogenation of oleic acid is 26.7 kcal/mole (245–270C). This appreciably higher activation energy is reflected in the higher temperature for the hydrogenation of oleic acid compared to the reduction of Cu^{2+}. This difference in activation energy between the formation of CuH and the hydrogenation of oleic acid indicates that the rate determining step is the reaction between CuH and the acid group; in consequence the reaction $CuOl + H_2 \longrightarrow CuH + HOl$ can reach equilibrium.

From the structure of CuH it may be expected that its solubility in oleic acid will be very poor. From literature it is known that CuH dissolves in pyridine by complex formation. It seems therefore reasonable to assume that the CuH is present as a complex with the acid group:



$$\begin{array}{c} OH \\ | \\ R - C - O \\ \vdots \quad \vdots \\ H - Cu \end{array}$$

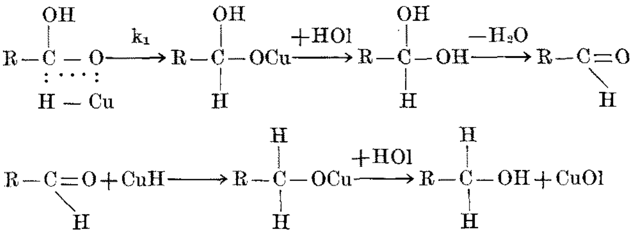
This assumption also explains the independence of

TABLE III

Continuous Hydrogenation of Fatty Acids and Fatty Oils Under the Influence of Cu and Cd Soaps

Hydrogenation of	Cu:Cd in % m	Feed, ml/h	Pressure in atm H_2	Temp, C	Conversion %	Selectivity %
Oleic acid	5:2.5	110	275	260	85	99
Oleic acid	5:2.5	150	230	260	79	99
Oleic acid	5:2.5	110	300	260	88	88
Oleic acid	5:2.5	146	300	260	88	89
Oleic acid	5:2.5	140	275	260	90	90
Capric acid	3:1.5	120	250	260	85	
Olive oil	5:2.5	110	200	260	60	90
Soybean oil	5:2.5	140	250	270	75	75
Linseed oil	5:2.5	180	300	270	70	70

the reaction rate of the acid concentration. The rate determining step could be the following reaction:



$$R-\overset{OH}{\underset{\vdots\cdots\vdots\;H-Cu}{C}}-O \xrightarrow{k_1} R-\overset{OH}{\underset{H}{C}}-OCu \xrightarrow{+HOl} R-\overset{OH}{\underset{H}{C}}-OH \xrightarrow{-H_2O} R-\underset{H}{C}=O$$

$$R-\underset{H}{C}=O+CuH \longrightarrow R-\overset{H}{\underset{H}{C}}-OCu \xrightarrow{+HOl} R-\overset{H}{\underset{H}{C}}-OH+CuOl$$

Following this scheme we arrive for the rate of the hydrogenation to the following equation:

$$v = k_1 [CuH\cdot HOl] = k_1K_1 [CuH] [HOl] = k_1K_1K_2 [Cu] [H_2].$$

This equation is in accordance with the first part of the experimentally found equation:

$$v = k [Cu] [H_2] \{ 1 + K [Cd] \}$$

For the last part of this equation no explanation can be offered.

The end conversion of the hydrogenation of oleic acid in hendecane as solvent is 67–70%. At higher conversions the reaction mixture becomes heterogeneous. This can be explained as follows: The alcohol, formed by the hydrogenation of the acid, reacts with the remaining acid under formation of an ester. When the conversion is higher than 50% an excess of free alcohol will be present. The excess of alcohol reacts with the soap by which reaction ester, metal oxide and water are formed:

$$\text{acid} + \text{alcohol} \rightleftarrows \text{ester} + \text{water}$$

$$\text{alcohol} + \text{soap} \rightleftarrows \text{ester} + \text{water} + \text{metal oxide}$$

If it is assumed that the equilibrium constants are independent of the solvent concentration and independent of the conversion, it can be calculated that the point at which the soap will react with the alcohol will shift to a higher conversion when less solvent is present, which is in accordance with the experiments. Moreover, the water concentration in the liquid phase will rise more than linearly with decreasing solvent ratio, thus shifting the equilibrium to the left.

The function of Cd-soap is not understood. It might be, however, that the Cd, e.g., as metal on the wall of the reactor and as soap in solution, stabilizes the CuH against decomposition into Cu and H_2.

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Lipid Oxidation in Flour Doughs—Observations Involving the Boron Trifluoride Interesterification Reaction

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Abstract

Lipid extracted from unyeasted wheat flour doughs had earlier yielded hitherto unidentified methyl esters using boron trifluoride interesterification when the lipid was isolated from aged or chemically oxidized flours or doughs. The identity of one unknown constituent is shown to be methyl methoxy stearate which could also be an artifact of the interesterification process. Conditions of formation of the artifact have been carefully studied and statistical analysis of the yields of this substance from the lipid of naturally aged flour doughs maintains our view of a reversible lipid oxidation stage being involved in natural and chemical flour maturing in the presence of oxidants in doughmaking.

Introduction

FLOUR TREATMENT involves oxidative reactions which can affect either the protein or lipid of flour. At the 6th I.S.F. Congress in London, 1962, we presented (1) the results of work on the lipids of flour dough in which unexpected changes were observed in the gas-liquid chromatograms of fatty acid ester mixtures prepared from dough lipids by the boron trifluoride/methanol interesterification reaction (2). Two unidentified compounds, designated x and y, were formed at the expense of the unsaturated fatty acids of the dough lipid, their appearance apparently being enhanced if an oxidant, potassium iodate, was added during dough mixing (Fig. 1). Subsequently we examined factors influencing the appearance of these compounds in ester mixtures and identified x and y