Copper Catalysts in the Selective Hydrogenation of Soybean and Rapeseed Oils: II. The Effect of a Hydrogen Flow Over Copper Chromite Catalyst

L.E. JOHANSSON and **S.T. LUNDIN**, Department of Chemical Technology,
Chemical Center, P.O.B. 740, S-220 07 Lund 7, Sweden

ABSTRACT

Time required for hydrogenation of soybean and rapeseed oils to 1-2% linolenate content with a copper chromite catalyst is reduced 40-60% if the dead-end system is replaced with a procedure using a flow of hydrogen through the reactor. The effect is ascribed to the removal of oxidation products, acting as catalyst poisons, and the water which is formed during reduction of the catalyst. Selectivity towards the linolenate compound is nearly unchanged.

INTRODUCTION

Advantages of hydrogenating soybean and rapeseed oils with a catalyst based on copper are high selectivity towards the linolenic compound (S_{Ln}) and nonexisting formation of saturates (1,2). The low activity of copper catalysts is well known. Typical S_{Ln} value of an industrial use nickel catalyst is 2-3, and its activity corresponds to more than 200 liter H_2 (STP)/hr/g Ni. Corresponding values of a typical copper-containing catalyst are 7-12 and 40 liter H_2/hr/g Cu, respectively (3). S_{Ln} values are then calculated as the ratio k_3/k_2 in the consecutive reaction scheme:

$$\text{Triene} \xrightarrow{k_3} \text{Diene} \xrightarrow{k_2} \text{Monoene} \xrightarrow{k_1} \text{Saturate}$$

Most copper-containing catalysts are composed of copper in its divalent state. The copper is partially reduced to metal during the hydrogenation.

When the copper of a hydrogenation run with 0.1 wt % Cu in the oil is reduced to metal, water is generated in an amount which corresponds to ca. 300 ppm water. Addition of 400 ppm water to a specially refined soybean oil reduces the rate of hydrogenation in a dead-end system to 70% (4). In the dead-end system, the reactor is supplied with as much hydrogen as the oil consumes, and dispersion of hydrogen gas is assisted by mechanical agitation. The water formed remains within the autoclave.

Konetzke et al. (5) reported the deactivating effect of water on the hydrogenation of fatty acids with copper chromite catalysts. Miya et al. (6) made use of a copper chromite catalyst in hydrogenation of fatty esters to higher alcohols. They studied the absorption of water on reduced catalyst at the pressure of 10 kp/cm^2. Water was adsorbed until equilibrium was reached on the catalyst surface. The adsorption resulted in deactivation of the catalyst.

The poisoning effect in connection with adsorption of water on the surface of reduced copper is thoroughly discussed in the literature. However, copper chromite catalyst also has high activity during the two periods of catalyst reduction (5) when water is being generated. The effect of water is thus of special interest in fat hydrogenation.

During hydrogenation, the surface layer of the copper chromite catalyst consists of a mixture of copper metal atoms and oxidic copper. Hydrogen spillover is quite possible between metal atoms and oxide at such a surface. Water has been found to enhance the conditions for dissociative adsorption of hydrogen in systems in which hydrogen spillover is assumed to occur. Boudart et al. (7) reported that yellow tungsten(VI)oxide, catalyzed by platinum black at room temperature, can be reduced by molecular hydrogen to form blue solids with a molar composition of $H_{0.35}WO_3$, if water was pre-adsorbed at the surface of the WO_3. They reported similar results in reduction of copper(II)oxide, though the CuO experiments were difficult ot evaluate because the reduction generated water. The co-catalyst water acts as proton acceptor and the transported species are the solvated protons (8).

We have found that the time required to reduce linolenate in soybean oil to ca. 1% is reduced if the dead-end system is replaced with a procedure combining the mechanical agitation of the dead-end autoclave with a limited flow of hydrogen through the oil. The resulting procedure is called "flow procedure." Results from hydrogenation using flow procedures have been published earlier (9), but without discussing the implications.

A flow of hydrogen gas through the oil and out from the autoclave may affect the conditions of hydrogenation by: (a) improving phase contact gas/liquid; (b) maintaining hydrogen pressure in the headspace; and (c) removing water and other catalyst poisons. These three effects and their consequences have been studied here. The dead-end procedure has been compared to flow procedures. Data in the comparison is given on the basis of the time required for an iodine value drop of 15 units, after which linolenic acid ester normally is reduced to ca. 1% in soybean oils and 1-2% in rapeseed oils.

EXPERIMENTAL PROCEDURES

Materials

Commercially refined and bleached soybean and rapeseed oils were hydrogenated. Percentage of erucic acid in the different rapeseed oils was ca. 17%. The Cu-1106P catalyst was obtained from Harshaw Chemical Co. (40% CuO, 47% Cr_2O_3, and 10% BaO). In experiments for mass spectrometric analyses, hydrogen gas of high purity was used (99.99%; 5 vpM H_2O, 3 vpM O_2, and 100 vpM N_2).

Analytical Methods

Methyl esters, prepared from oil samples with sodium methylate catalyst and dimethyl carbonate, were analyzed with a 9 ft. x 1/8 in. stainless steel column packed with 7% BDS on 80/100 Chrom W and a flame ionization detector. Iodine values were determined according to the Wijs method. The percentage of conjugated dienes was calculated from the UV absorption at 232 nm. The amount of crystalline copper metal in the catalyst samples was determined from X-ray diffraction analyses with the barium chromate phase as internal standard (10).

The percentage of isolated trans was estimated by IR absorption in carbon disulphide with methyl elaidate as the standard.

Mass spectroscopic analysis of gas streams was carried out with an AEI MS 10 mass spectrometer with a continuous inlet system. Gas to be analyzed was introduced through a heated capillary. The pressure of the analyzer tube was $2 \cdot 10^{-6}$ Torr, and a scan from m/e 12 to m/e 45 or from m/e 36 to m/e 200 was performed in 11 minutes.

The amount of water in the gas was estimated on the basis of the ratio between the peaks at m/e 17 and m/e 15.

The signal at m/e 17 represented water with the relative intensity of 23% (m/e 18 = 100%).

Equipment and Operating Procedures

The hydrogenation procedure in the 1 liter Parr apparatus was described earlier (10). In the normal procedure, 300 g of oil was hydrogenated at a stirrer rate of 1700 rpm and at a temperature of 185 C. The hydrogen flow through the oil was measured after passing through the outlet valve at 1 atm and 20 C. No hydrogen was recirculated.

RESULTS AND DISCUSSION

Transfer of Hydrogen

In order to enable a direct observation of the stirrer function, a copy of the reactor cylinder was made of transparent material. The stirrer was rotated and a flow of hydrogen was led through the oil at room temperature and atmospheric pressure. The amount of oil was varied at two levels, 300 and 600 g.

Cooling coils, stirrer-bearer, and sampling tube caused vigorous turbulence within the oil phase. At 700 rpm, the entire oil bulk was filled with bubbles, 0.5 - 2 mm in diameter. At 1700 rpm, the oil was thrown into the headspace and the enclosed gas was effectively changed. The contact between the oil and gas phases was more effective with 300 g at 1700 rpm than with 600 g at 700 rpm, but under no circumstances did a flow of 50 liter H_2/hr influence the picture of bubbles in the oil bulk.

In the dead-end hydrogenations, a rate of hydrogenation was independent of the stirrer rate in the interval 700-1700 rpm. A further increase of the interface gas/liquid caused by a hydrogen flow of 50 liter/hr through the oil did not improve the conditions of mass transfer in the processing of 300 g oil at 1700 rpm.

An estimation of the resistance of external hydrogen transfer was performed on the basis of the film model. The hydrogen transfer of the film gas/oil was studied according to the procedure described by Pihl and Schöön (11) under the conditions of a typical copper hydrogenation: 185 C, 3 atm, 300 g soybean oil, 1700 rpm, 50 liter H_2/hr. However, a pre-reduced nickel catalyst was used to avoid the reduction stages of the copper catalyst. The volumetric mass transfer coefficient k_La was found to be 0.65 sec^{-1}.

The mass transfer coefficient k_H for the transport of hydrogen from the oil bulk to the external sruface of the catalyst particles was estimated on the basis of the results of Levins and Glastonbury (12) according to the calculation procedure given by Bern et al. (13). The mean particle size of the Cu-1106P used was determined to be $2.2 \cdot 10^{-3}$ cm (14). The power number N_P of the impeller was estimated as 2 (12), resulting in a specific power group 0.96. The coefficient k_H was estimated as 0.42 $cm \cdot sec^{-1}$.

The concentration differences over the two films were calculated for a series of Cu-1106P hydrogenations (Table I). The maximum concentration difference of the film near the gas bubbles was less than 6% of the hydrogen solubility. The concentration difference of the film between the oil and the catalyst particle was negligible.

TABLE I

Hydrogen Concentration Differences of the Two Transport Films in Copper Chromite Hydrogenations

% Cu	$N \cdot 10^3$ Mole $(1 \cdot sec)^{-1}$	$\frac{(\Delta c)_1}{c_o{}^a} \cdot 10^2$	$\frac{(\Delta c)_2}{c_o} \cdot 10^2$
0.050	0.208	1.2	0.6
0.075	0.510	3.0	0.9
0.100	0.655	3.9	0.9
0.200	0.988	5.8	0.7

[a] $c_o = 2.58 \cdot 10^{-2}$ mole/1 at 185 C and 6 atm.

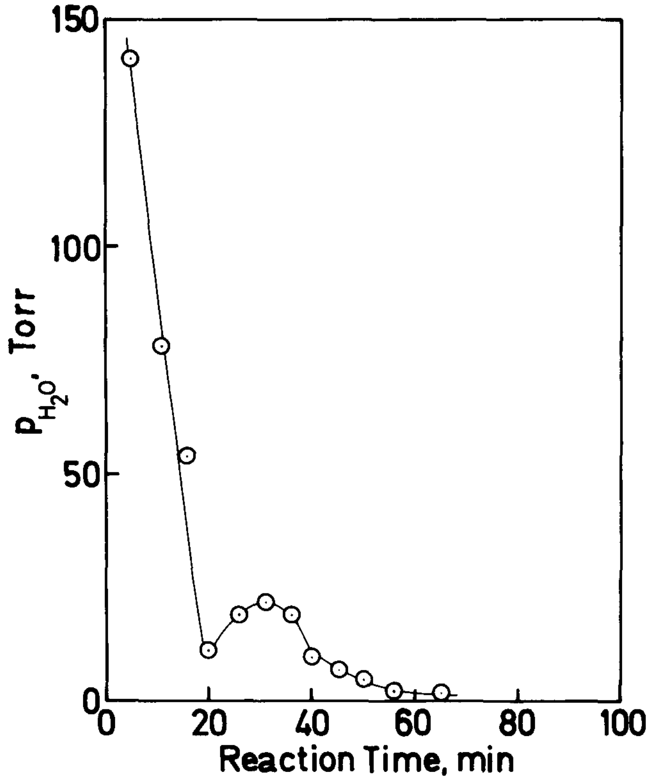

FIG. 1. Water content of the outlet flow in hydrogenation of rapeseed oil with Cu-1106P catalyst (0.2 wt %, 6 atm, 185 C, and 50 liter H_2/hr).

Dilution Effect of the Reduction Water

If the copper in the copper-containing catalyst, which is supplied to the oil in its divalent state, is completely reduced, 0.16 mole of water is generated per kg oil and percentage unit Cu in the oil (wt %). Provided that all water formed is transferred to the gaseous phase, the maximum hydrogen dilution due to the reduction of the catalyst may be estimated from the expression

$$-\Delta p_{H_2} = p_{H_2O} = C_{Cu} \frac{m_{oil}}{V_{hs}} \cdot 0.16\ RT \qquad 4.$$

where $-\Delta p_{H_2}$ = decrease of the hydrogen pressure, atm, p_{H_2O} = partial pressure of water, atm, C_{Cu} = wt % Cu in the oil, m_{oil} = amount of oil in the autoclave, kg, V_{hs} = volume of the headspace, liter, R = 0.082 liter atm $mole^{-1} K^{-1}$, and T = temperature, K.

The effect of hydrogen pressure on the rate of hydrogenation will be discussed in the following paper. Here an approximate correlation is sufficient between time required for an iodine value drop of 15 units, t_{15} min, and hydrogen pressure p_{H_2} atm (approximately equal to the total pressure P atm at flow hydrogenations). For pressures between 2 and 6 atm the time t_{15} can be written:

$$t_{15} = t_{15}^* + \frac{t_{15}}{4} (6 - P) \qquad 5.$$

Here the time t_{15}^* is determined from a hydrogenation run at the 6 atm pressure with C_{Cu} wt % Cu in the oil. The maximum effect of hydrogen dilution due to the reduction water is obtained from equations 4 and 5:

$$\Delta t_{15} = t_{15} - t_{15}^* = \frac{t_{15}^*}{4} (-\Delta p_{H_2}) \qquad 6.$$

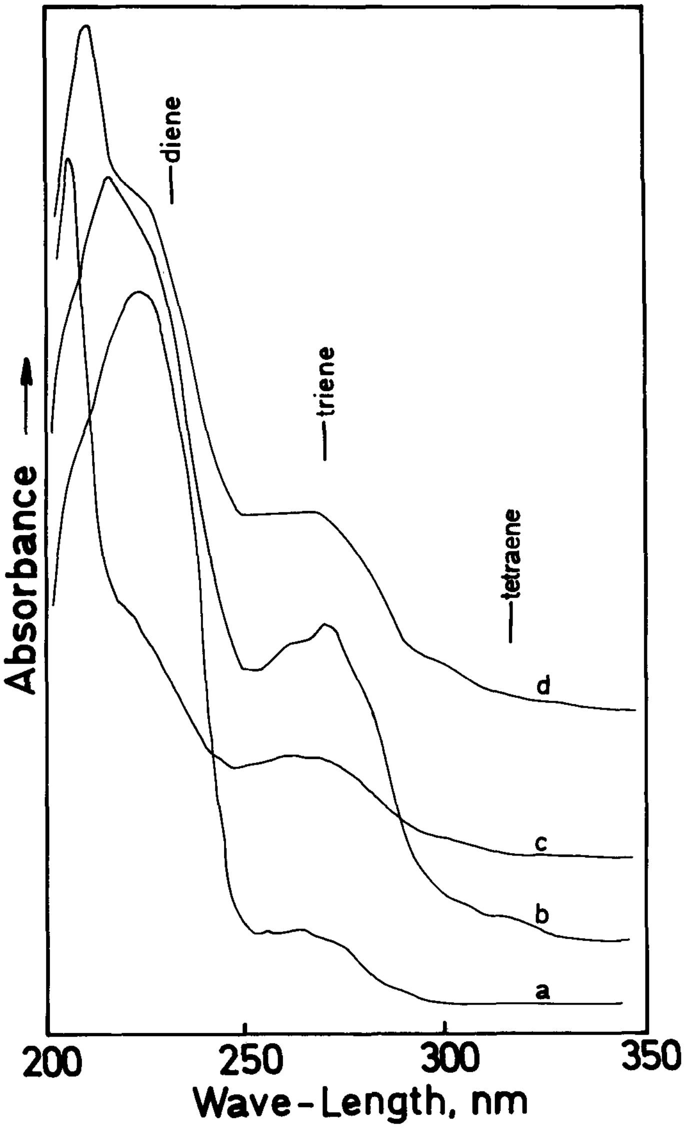

FIG. 2. UV absorption spectra from condensates (soybean oil); (a) degassing at 90 C and 2 Torr; (b) N_2 stripping at 185 C and 40 Torr; (c) heating-up period; (d) hydrogenation after degassing and N_2 stripping (0.1 wt % Cu, 6 atm, 185 C, and 50 liter H_2/hr).

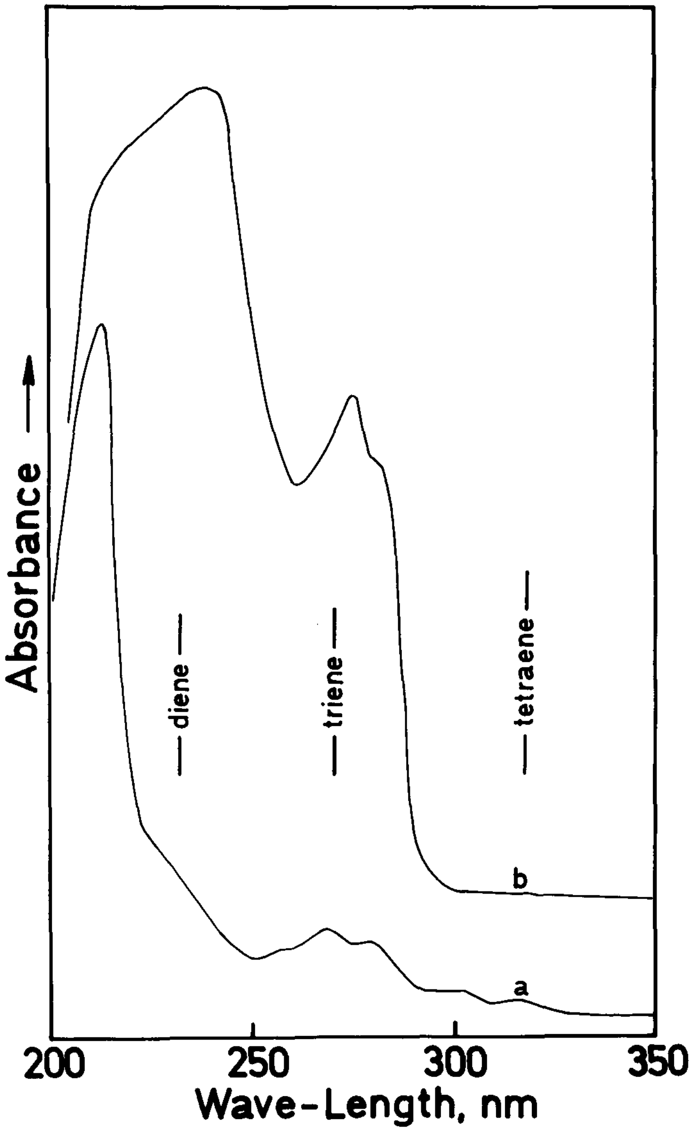

FIG. 3. UV absorption spectra from (a) original technically refined soybean oil and (b) the condensate from a hydrogenation run without special pretreatment of the oil.

$$\Delta t_{15} = C_{Cu} \cdot \frac{t_{15}^{*}}{4} \cdot \frac{m_{oil}}{V_{hs}} \cdot 0.16\ RT \qquad 7.$$

In a typical hydrogenation run in the Parr apparatus (C_{Cu} = 0.1 wt %, t_{15}^{*} = 30 min, m_{oil} = 0.3 kg, V_{hs} = 0.57 liter, and T = 458), the prolonging effect of hydrogen dilution at dead-end hydrogenation is on the order of 2 min. With 0.6 kg oil in the bomb (m_{oil}/V_{hs}), reaction time increases by 13 min.

Mass Spectrometric Analyses of the Gas Stream

Volatile substances, which leave the oil with the hydrogen flow, exist either in the bleached oil or are generated during the process. Mass spectrometric analyses of the gas stream from the autoclave were performed during rapeseed oil hydrogenation, because these oils normally contain more catalyst poisons than soybean oils. Water vapor and carbon compounds with up to six or seven carbon atoms were detected. The spectra obtained have not been studied in detail. No other compound was found with the possible exception of substances concealed within the groups of signals representing the carbon chain fragments. In particular, no hydrogen sulphide was detected. In that respect, the result was confirmed by leading the outlet gas of several hydrogenation runs through a zinc acetate solution, which was analyzed according to the procedure described by Gustafson (15).

MS analyses of the outlet gas flow from the autoclave during flow hydrogenations included estimation of the water content of the gas. Reduction water leaves the oil in two periods, reflecting the two periods of catalyst reduction (Fig. 1). The maximum partial pressure of water in headspace during a run at 6 atm with 2 g of Cu-1106P catalyst is ca. 140 Torr (0.19), and the mean value of the second period of catalyst reduction and water removal corresponds to ca. 15 Torr.

Organic Compounds in the Hydrogen Stream

Organic compounds leaving the autoclave with the hydrogen flow were isolated as follows: 300 g of soybean oil was purified from volatile substances in two steps. To remove air oxygen and other dissolved gases, the oil was heated at 90 C and 1-2 Torr for 40 min. In the second step, the oil was stirred at 185 C while continuously flushing it with nitrogen, which contained less than 10 vpM O_2 (20-40 Torr and ca. 10 liter N_2/hr.) One gram of Cu-1106P

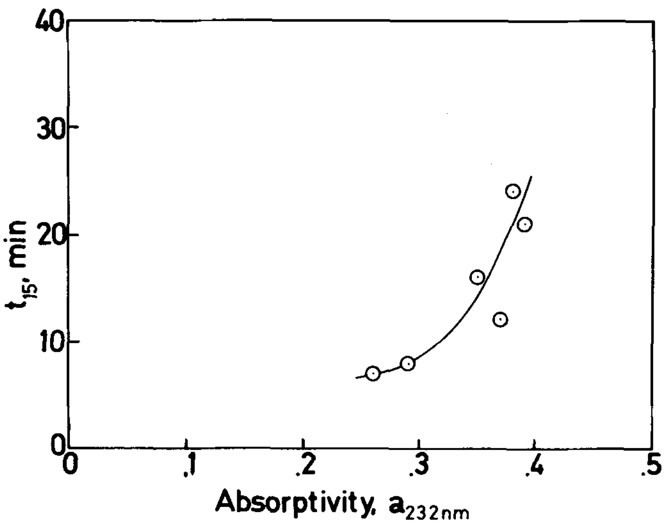

FIG. 4. Time for an iodine value drop of 15 units vs. absorptivity $a_{232\ nm}$ for 6 soybean oils (Cu-1106P, 0.2 wt % Cu in the oil, 6 atm, 185 C and 50 liter H_2/hr).

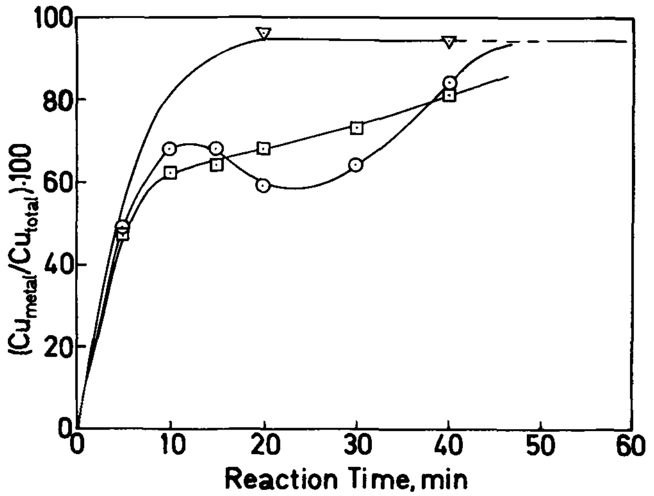

FIG. 5. Copper metal in Cu-1106P catalyst during hydrogenation of soybean oil at 3 atm and 185 C (X-ray diffraction analysis): □ Dead-end, ○ 50 liter H_2/hr, and △ addition of water to the inlet flow, 50 liter H_2/hr.

catalyst was added and the oil was hydrogenated at 185 C and 6 atm H_2 pressure according to the normal procedure which included a heating up period. The flow of gas leaving the oil during the two purification steps, the heating up period prior to the hydrogenation, and the hydrogenation was led through cold traps with liquid nitrogen. The four condensates, with the exception of the oil drops situated in the heads of the cold-traps, were dissolved in iso-octane (spectrograde). The solutions, which gave off a strong odor, were subjected to UV absorption analysis (Fig. 2).

The spectrum of the first condensate showed two distinct maxima, indicating the presence of a conjugated compound. Conjugated dienes, trienes, and tetraenes left the oil during the N_2 stripping. Spectra obtained from these condensates showed oxidation products formed during the bleaching process (16). Such compounds were present in the oil (Fig. 3) and normally, when no nitrogen stripping at 185 C occurred, these compounds were found in the hydrogen flow leaving in the autoclave. With nitrogen stripping, the UV absorption spectrum from the hydrogenation step did not show the clear maxima from the conjugated trienes, but rather the dienes dominated. On the whole, the condensate showed a smaller absorption of conjugated dienes and trienes in comparison to the peak at 220 nm.

In Figure 4, the time required for an iodine value drop of 15 units for seven soybean oils was plotted vs. the UV absorption at 232 nm. Obviously, preconjugation had a negative effect on the rate of hydrogenation.

The poisoning effect of oxidation products was studied by addition of 1 g of selenium dioxide (0.009 mole) to soybean oil, together with the catalyst. Conjugation occurred, resulting in a UV absorption spectrum similar to that of the condensates during the nitrogen stripping. With the exception of some initial reduction of the iodine value, the catalyst poisoning was total. To evaluate the total poisoning effect of volatile components, including water, the condensate from a normal flow hydrogenation of rapeseed oil (1 g of Cu-1106P, 6 atm, 185 C, and 50 liter H_2/hr) was added to 300 g of easily hydrogenated soybean oil, prior to a dead-end hydrogenation. The time required for an iodine value drop of 15 units increased from 23 to 85 min.

TABLE II

Effect of Nitrogen Stripping (Cu-1106P, 0.2 wt % Cu in Rapeseed Oil, 6 atm, and 185 C)

Pretreatment	Procedure	Time Δ(IV) = 15 min
Normal	Dead-end	133
N_2-stripping, 1 hr, 40 Torr, and 185 C	Dead-end	76
Normal	Flow	71
N_2-stripping, 1 hr, 40 Torr, and 185 C	Flow	29

The effect of nitrogen stripping on the hydrogenation of rapeseed oil is shown in Table II. The principal difference between the dead-end and the flow procedures was not affected.

Water of the Catalyst Reduction

Water generated during stoichiometric reduction of the divalent copper in the Cu-1106P catalyst and transferred to the headspace of the autoclave corresponds to ca. 0.3 atm/g catalyst (185 C, 300 g oil, and a gas volume of 0.57 liter). In the case of a dead-end hydrogenation, the partial pressure of water is built up gradually, while the initial stage, in many respects, is similar to that of a flow hydrogenation.

Figure 5 shows the course of copper metal formation during a dead-end hydrogenation run. The marked second period of copper formation was considerably weaker than that of flow hydrogenation (10).

The inlet hydrogen gas of a flow hydrogenation with 1 g of catalyst (0.1 wt % Cu) was saturated with water at 55 C. Thus, the partial pressure of water in the gaseous phase in the autoclave was at least 0.15 atm during the whole process, even if the process in all other respects was a typical flow hydrogenation. The total pressure was adjusted to 3.15 atm. The catalyst reduction proceeded in one step (Fig. 5), apart from the reduction of a normal flow hydrogenation. Obviously, the presence of water favors the catalyst reduction which is in accordance with the results of Boudart et al. (7).

The influence of water upon the catalyst reduction can be summarized as follows: a moderate water concentration in the oil phase favors the reduction process, while too much water retards it. In a flow hydrogenation, water

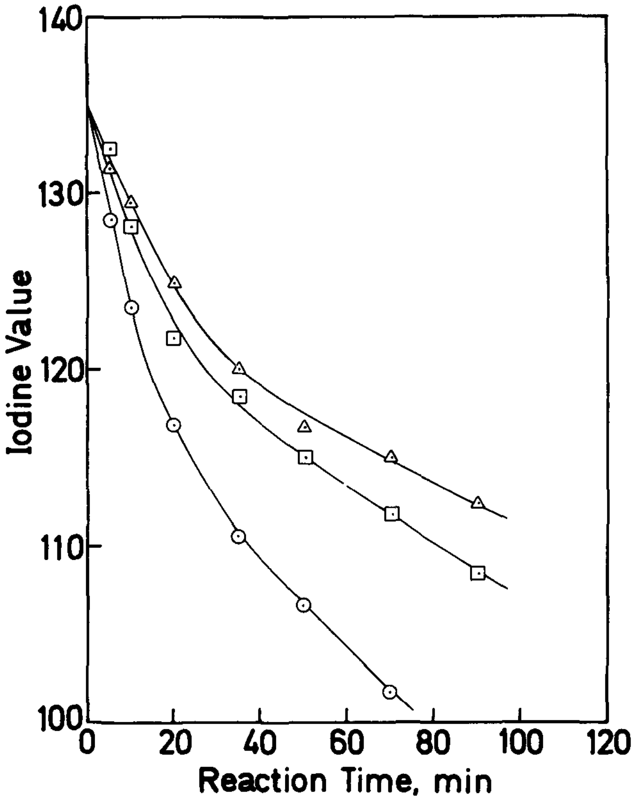

FIG. 6. Hydrogenation of soybean oil with Cu-1106P catalyst (0.1 wt % Cu in the oil at 3 atm and 185 C): □ Dead-end, ○ 50 liter H_2/hr, and △ addition of water to the inlet hydrogen flow of 50 liter H_2/hr.

formed is continuously removed from the autoclave. The reduction ceases when the main part of the catalyst has been reduced to metal.

The iodine value graphs of the dead-end and the two flow hydrogenations are shown in Figure 6. The rate of reaction -d(IV)/dt is high during catalyst reduction, which is in accordance with the results presented earlier (10). When the reduction is finished (the flow hydrogenations only), the rate of reaction is lower in the presence of water than in its absence. The fully reduced catalyst is poisoned by water.

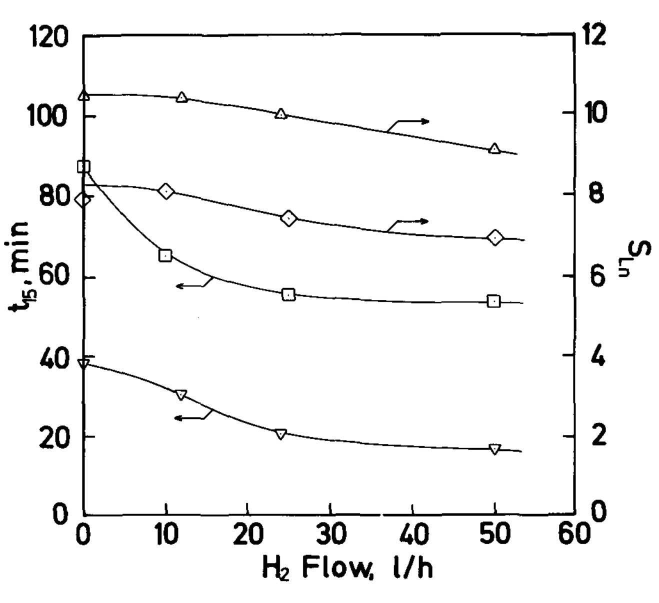

FIG. 7. Hydrogenation time and selectivity S_{Ln} vs. the hydrogen flow (Cu-1106P, 0.2 wt % Cu, 6 atm, and 185 C): Soybean oil ▽ and △, respectively; rapeseed oil □ and ◇ resp.

Comparison between Dead-End and Flow Procedures

The effect of a hydrogen flow on hydrogenation time t_{15} and selectivity towards the linolenate compound is shown in Figure 7. Table III shows the composition data for the experiments represented in the figure. Maximum effect is obtained at a hydrogen flow of 50 liter/hr, corresponding to a gas load of 155 liter H_2 (STP)/hr/kg oil. The time required for an iodine value drop of 15 units was reduced by 40-60% of the time in the dead-end procedure.

Maximum content of conjugated dienes in the oil is lower during a flow hydrogenation even if the final product composition, in this respect, does not show any great difference. Selectivity S_{Ln}, calculated according to the program given by Butterfield and Dutton (17), decreases with increasing hydrogen flow, but the total change is small. The amount of *trans* isomers formed is practically independent of the hydrogen flow.

The lower S_{Ln}-values noted for rapeseed oil are consistent with the product composition reported by

TABLE III

The Effect of a Hydrogen Flow on the Hydrogenation Product (Cu-1106P, 0.2 wt % Cu in the Oil, 6 atm, and 185 C)

Oil	Flow 1/hr	Reaction time min	IV (Wijs)	GLC Composition C18:0 %	C18:1 %	C18:2[a] %	C18:3[b] %	trans %	Conj. dienes %	S^c_{Ln}
Soybean oil	---	---	131.5	3.8	22.1	53.0	8.2	---	0.1	---
	0	35	117.0	3.8	32.6	49.9	1.1	14.2	0.6	10.3
	12	35	114.6	4.0	33.8	48.9	0.8	14.4	0.8	10.4
	24	20	116.0	3.9	32.8	49.1	1.0	14.4	0.6	10.0
	50	20	113.3	3.7	34.8	47.9	1.1	11.0	0.9	9.1
Rapeseed oil	---	---	111.4	1.1	36.0	19.6	10.8	---	0.2	---
	0	90	96.0	1.1	40.4	22.7	2.4	11.4	0.3	7.5
	10	70	95.6	1.2	41.9	22.7	1.3	11.7	0.3	8.1
	25	50	96.8	1.1	41.0	23.0	2.4	10.8	0.4	7.4
	50	50	96.7	1.1	41.0	22.6	2.1	11.4	0.4	6.7

[a] Does not include conjugated dienoates.

[b] Includes conjugated dienoates.

[c] Calculated from the GLC compositions.

Jakubowski and Pezinski (9).

The flow procedure allows a better utilization of the copper charged. The industrial application corresponds to a system using hydrogen recirculation, including a purification train, dimensioned for a water uptake of ca. 0.3 kg water/kg copper in the catalyst.

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