Catalyst Studies for Hydrogenation of Vegetable Oils

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Abstract

Cottonseed and soybean oils were partially hydrogenated using various commercial nickel catalysts. Methods were investigated by which commercial catalysts can be changed with respect to the rate of reaction, selectivity or *trans*-isomerization during hydrogenation of the oils. Catalysts which were treated with hydrogen sulfide produce considerably more *trans* isomers but catalysts treated with air often cause higher selectivity ratios. Factors affecting the hydrogenation characteristics of a catalyst are discussed.

When triglyceride oils are partially hydrogenated, the overall rate of hydrogenation, selectivity ratio and the isomerization level are all factors of industrial importance. Each of these factors can be controlled independently to at least some extent in commercial hydrogenators, by varying the operating conditions such as temperature, hydrogen pressure, agitation and the catalyst concentration. These operating variables have previously been investigated and the role of each has been explained based on the controlling steps in the process (1,3,5,9,11,15). In many if not all commercial batch reactors, the step which is most controlling is the transfer of the hydrogen to the liquid phase.

Variations in the type of nickel catalysts used for hydrogenation of vegetable oils have received however much less attention. The technique of catalyst preparation, formulation, particle size, pore size and pore size distribution, and even the type of carrier or additives, if used, are known to be important to at least some extent (10,13,14). The catalyst activity as well as its characteristics in determining selectivity and isomerization is also influenced by the materials that cause partial poisoning of the catalyst. Bailey (9) mentions the influence of hydrogen sulfide on nickel catalyst. Such a treatment of the catalyst is claimed to increase the isomerization and to decrease selectivity. Albright *et al.* (4) investigated used catalysts and also treated a nickel catalyst with air, vacuum, hydrogen or steam. As a result of these treatments, some of the characteristics of hydrogenation were changed in runs made at 130 C.

In the present investigation the nickel catalysts were treated with both air and hydrogen sulfide. Also several additives were tested to determine their effect on selectivity and on geometrical isomerization during hydrogenation.

Experimental Procedures

The hydrogenation equipment and procedures used were essentially identical to those employed previously by Wisniak and Albright (15). The dead-end hydrogenator had a capacity of ¾ gal, was provided with a turbine-type impeller and was heated by hot oil circulating through its jacket.

Gas chromatography, using an Aerograph 202 unit, was employed to determine the fatty acid group composition of the hydrogenated samples. The results obtained were corrected for nonuniform thermal detector response by applying factors of Pons and Frampton (12). The *trans*-isomer content was measured using a Beckman IR-8 infrared spectrophotometer and employing a secondary standard of trielaidin (Robert O'Connor, Chairman of the Spectroscopy Committee of AOCS). Both methods of analysis were essentially similar to the ones recommended in the Official and Tentative Methods of AOCS (8). Statistical analysis indicated that the results obtained here were accurate to within 5% on a relative basis except for those components present in very low concentrations.

Nysel, Rufert flakes, "old Rufert flakes" which had been obtained in 1953, and G-15 catalyst were used in this investigation. Nysel and G-15 catalysts are of the supported type and are produced by dry-reduction. Rufert flakes however are unsupported and produced by wet-reduction. The Harshaw Chemical Co. manufactured the Rufert flakes and Nysel catalyst, and the Girdler Catalyst Department of the Chemetron Corp. produced the G-15 catalyst. The catalysts were in some cases pretreated by bubbling either air or hydrogen sulfide through agitated oil-catalyst suspensions in a three-neck flask at 100 C.

The hydrogen employed contained 0.5% or less oxygen. Refined and bleached oils (Anderson, Clayton & Co.) were used in this investigation. The cottonseed oils had iodine values from 111 to 116; these values were calculated based on the composition of the unsaturated fatty acid groups in the oil. The soybean oil had an iodine value of 134.8.

Experimental Results

Forty hydrogenation runs were made with cottonseed oil and 15 runs with soybean oil. The operating conditions were in the following ranges. Temperature: 142–170 C (controlled within ± 2.5 C during the initial stages of the run and within ± 1 C during the remainder of the run); pressure: 40 ± 1 psig for runs with cottonseed oil, 60 ± 1 psig for runs with soybean oil; agitation: 1750 ± 20 rpm as measured by a stroboscope; catalyst concentration: 0.05 weight per cent nickel for runs with cottonseed oil, 0.10 weight per cent nickel for runs with soybean oil.

During most runs, five to six oil samples were obtained at intervals of about 10–15 iodine value (IV) units. The logarithm of IV was plotted versus the time of sampling, and the best smooth curve was then

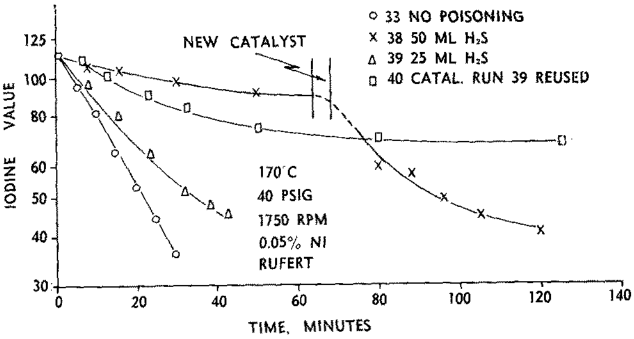

FIG. 1. Effect of treating Rufert catalyst flakes with hydrogen sulfide: rate of hydrogenation for runs with cottonseed oil.

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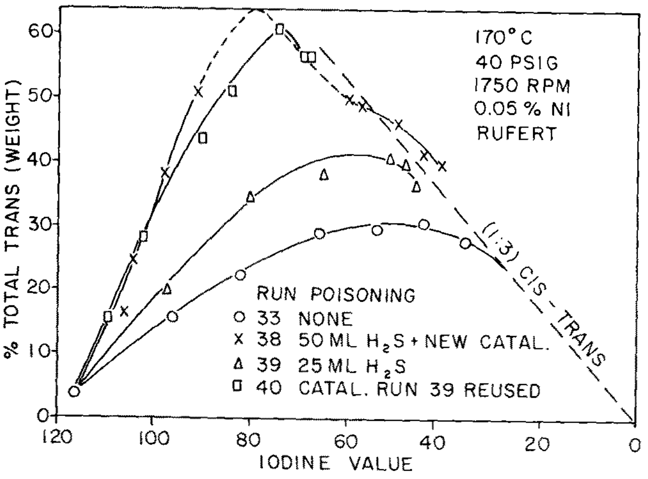

FIG. 2. Effect of treating Rufert catalyst flakes with hydrogen sulfide: *trans*-isomerization for runs with cottonseed oil.

drawn. As a rule, this curve fit the experimental data well, as indicated by Fig. 1. In general, the overall rate of hydrogenation for any run (at constant temperature, pressure, rate of agitation and amount of catalyst) was represented reasonably well by the following first order equation:

$$\text{rate} = -\frac{d(IV)}{dt} = k\ (IV)$$

The integrated form of this equation is:

$$\ln \frac{(IV)\ \text{initial}}{(IV)_t} = kt$$

The pseudo reaction rate constant $\min^{-1}$, k, generally did not vary significantly in value during the entire run. A similar finding has also been reported in the past (1,9,15).

Catalyst Comparison

The hydrogenation results for cottonseed oil runs are compared in Table I for the four catalysts used. The overall hydrogenation rate and hence also rate constant, k, were highest using Rufert flakes at both 150 and 170 C. Lower rate constants were found in decreasing order for Nysel, G-15, and old Rufert flakes. The k values decreased somewhat as the run progressed especially for runs using either G-15 or Nysel as catalysts, but less so for runs using Rufert flakes. The range of iodine values over which k values were determined is reported in Table I.

Plots were also made of the total diunsaturated acids (linoleic and other isomers) and of the total monounsaturated acids (oleic and other isomers) versus the iodine value. The best smooth lines were drawn in each case, and these plots were then used to determine the selectivity ratio (SR) as defined by Albright (2). At 150 C, Nysel catalyst resulted in the highest selectivity ratios and G-15 catalyst was next highest. Rufert flakes and old Rufert flakes resulted in the lowest selectivity ratios. At 170 C, no substantial differences in selectivity were found for the three catalysts tested.

Plots were also made of the amount of *trans* isomers as a function of the iodine value, as shown in Fig. 2. The amount of *trans* isomers formed was similar in runs using either G-15, Nysel or Rufert flakes. The maximum weight per cent of *trans* isomers formed during the course of a run is reported in Table I as Trans Max. A small increase in the *trans* isomers content was noted as the temperature was increased from 150 to 170 C. The smallest increase of isomerization with temperature occurred when G-15 was used. Old Rufert flakes were used only at 150 C and resulted in less *trans* isomers, as compared to the other three catalysts.

The differences found in the performance of the four catalysts are believed to be caused by differences in the method of preparation, formulation, age and physical structure. Coenen et al. (10) and Riesz and Weber (13) have both reported on the importance of the physical structure. They indicate that the pore size distribution and the average pore size of the catalyst affect selectivity. Steric effects also are a factor relative to isomerization during hydrogenation. Transfer of hydrogen and of unsaturated groups into the catalyst pores is important relative to the selectivity ratio and the degree of isomerization (3). Catalysts with considerable surface available in the pores are expected to be less temperature dependent relative to both selectivity and isomerization.

Catalyst Poisoning With Hydrogen Sulfide

Figures 1 and 2 indicate the effects of treating Rufert flakes with hydrogen sulfide. As shown in Figure 1, increased treatment of the catalyst resulted in progressively slower hydrogenation of the cottonseed oil. In Run 33, in which the catalyst was not treated (poisoned), the k value was large and essentially constant throughout the run after a short induction period (IP) as measured by the method used by Wisniak and Albright (15) at the beginning of the run. The constant k values resulted as indicated by the straight line relationship of the logarithm of IV versus time. The k values of Runs 38 and 39 not only were less because of the treatment of the catalyst with hydrogen sulfide, but the values decreased as the run progressed, as indicated by the non-linear correlations shown on Figure 1.

TABLE I

Comparison of Catalysts
Cottonseed Oil Batch 2 1750 rpm, 40 psig, 0.05% Nickel

Run number	Temp C	Catalyst	k($\min^{-1}$)	IV range	IP min.	Trans Max	SR	
							60 IV	70 IV
16	150	Rufert flakes	0.026	92–18	3	27	6.5	7
20	150	Rufert flakes	0.027	110–17	0	27	6.5	7
21	150	Nysel	0.026	100–60	1.5	27	11	10
			0.017	46–29	....	......	......	......
22	150	G-15	0.015	100–59	3	28	9	8.5
			0.010	45–40	....	......	......	......
23	150	Old Rufert flakes	0.006	88–42	36	25	5	5
27	170	Nysel	0.035	100–45	0	30.5	20.5	24
			0.029	34–29	....	......	......	......
28	170	G-15	0.035	110–90	0	29.5	23	24.5
			0.012	62–56	....	......	......	......
			0.003	45–40	....	......	......	......
29	170	Rufert flakes	0.038	100–28	1	31	20	22

Run 38 was performed in two stages. After the first stage of 64 minutes, in which a catalyst poisoned with 50 ml hydrogen sulfide was used, an iodine value of 87 was attained. A total of 0.05% (based on the weight of the initial oil) of fresh catalyst was then added to the system. As shown in Figure 1, the rate constant on Run 38 was then initially high but it too decreased as the run progressed. This result may have been caused by hydrogen sulfide remaining in the oil or by the migration of weakly adsorbed hydrogen sulfide on the initial portion of the catalyst to the highly active surface of the fresh catalyst.

Figure 2 indicates that *trans*-isomerization was increased very substantially because of the poisoned catalyst. In Run 38, the *trans* isomer content was about double to that of Run 33. The *cis*-to-*trans* isomer ratio approached 1:3 or perhaps even 1:4 as the run progressed.

The selectivity ratios of this series of runs varied at most from about 6 to 8, and they were not significantly changed because of the hydrogen sulfide treatments of the catalysts. The lengths of the induction periods were also similar in all of these runs.

Hydrogenation results for soybean oil using G-15 catalyst indicated a comparable decrease in rate constants when the catalyst was poisoned with hydrogen sulfide. Furthermore an increase in *trans*-isomerization also resulted. Even though the soybean oil runs were less reliable because they were rather preliminary in nature, the results were similar to those for runs using cottonseed oil and Rufert flakes.

When either Rufert flakes or G-15 catalyst was treated with large amounts of hydrogen sulfide, no significant hydrogenation of either cottonseed or soybean oil was obtained using these catalysts. A small increase in the *trans* isomer content was noted for both oils however.

The hydrogenation-dehydrogenation mechanism postulated by Allen and Kiess (7) was used to explain the results of these runs using hydrogen sulfide-treated catalysts. If two adjacent active sites on the catalyst are needed for hydrogenation, poisoning the catalyst with hydrogen sulfide may destroy one site of the pair. As a result, the fraction of isolated sites effective for isomerization but quite ineffective for complete hydrogenation increases significantly. Since selectivity was not affected by hydrogen sulfide treatment of the catalyst, the active sites remaining after poisoning were apparently not changed relative to the selective sorption of the unsaturates.

Catalysts Treated With Air

Table II summarizes the results for several runs which were made to determine how air-treated catalysts affect the hydrogenation of cottonseed oil. These runs were made at 170 C using Rufert flakes as the catalyst. In general the rates of reaction and the degree of *trans*-isomerization did not change significantly as compared to the results of runs with untreated catalysts. However the selectivity ratio tended to increase with additional air treatment.

The air treatment of the catalyst apparently changed the portion of the surface that adsorbs the unsaturates but it did not affect the active sites of the catalyst that actually produce hydrogenation and *trans*-isomerization.

Reused Catalysts

A catalyst treated with hydrogen sulfide was used in one run (Run 39) and then reused in the next (Run 40), and the results are shown in Figure 1 and 2. A catalyst which was treated with air was also used in successive runs. The loss of catalyst (by withdrawal of the samples and handling operations) was compensated by adding 5–6% new catalyst based on the amount used originally. In these runs, the second run of the series had a rate of reaction which was about 40% and 90% respectively that of the first run of the series. However, the selectivity of the second run with the air-treated catalyst was similar to the selectivity for runs with untreated catalysts. In the case of the catalyst treated with hydrogen sulfide, *trans*-isomerization was very high reaching a maximum of 60% *trans* isomers or even higher for the second use of the catalyst (see Figure 2).

TABLE II

Effect of Contacting Rufert Flakes With Air[a]

Run number	k, min^{-1}	IP min	Trans Max, %	Selectivity ratio			Air flow, time (12 cu ft/hr)
				60 IV	70 IV	80 IV	
33	0.041	2	30.5	6.5	6	6	None
34	0.037	3	30.5	6.5	6.5	6.5	Probably small
35	0.041	2	32.5	10	10.5	11	7 min
36	0.038	2	32.5	13	15	19	20 min

[a] Hydrogenation runs for cottonseed oil at 170 C.

Effect of Additives

Several materials which have been shown in the past to increase the rates of at least certain types of hydrogenations (10,13,14) were added to the reaction system as granular powders. Alumina (η type) was added for several runs in quantities up to 0.4% by weight based on the oil used. The resulting k values for these runs at both 150 and 170 C were about 15% to 20% higher than those for runs without alumina. No changes were noted however for the selectivity ratio or the degree of isomerization because of the alumina added. It had been hoped that the rates would have increased several fold when alumina was added just as it had for the hydrogenation of ethylene (14). The role of the alumina in the present investigation is not known, but it may have acted to remove catalyst poisons from the oil or hydrogen.

When calcium hydride and molybdenum trioxide were tested as additives, no appreciable changes in the type of hydrogenation were noted.

Comparison of Cottonseed Oils

When the results for Runs 29 and 33 made at the same operating conditions but with different batches of cottonseed oil were compared as shown in Table III, the rates of reaction and the degrees of isomerization were similar. Run 29 however resulted in a much more selective degree of hydrogenation. The oil used in Run 29 initially had a more intense coloration than that used in Run 33, but the hydrogenated product of Run 29 was lighter. Allen (6) has suggested that variations in the gossypol content of the oils may be responsible for the selectivity differences noted.

TABLE III

Hydrogenation Results for Two Different Batches of Cottonseed Oil[a]

Run number	Cottonseed oil batch	k, min^{-1}	IP min.	Trans Max, %	Selectivity ratio		
					60 IV	70 IV	80 IV
29	2	0.038	1	31.0	20	22	33
33	3	0.041	2	30.5	6.5	6	6

[a] Runs at 170 C.

Results

The hydrogenation temperature is important for runs made with air-treated catalysts as indicated by results of this investigation and those reported earlier at 130 C (4). At the lower temperature, the treated catalysts were found to be significantly deactivated, but such a deactivation was not present at 170 C. This finding indicates that the nickel catalysts were activated by hydrogen during the initial stages of hydrogenation at 170 C but to a lesser extent at 130 C. Earlier (4), unused but relatively old and inactive Rufert flakes were found to become activated during the initial stages of hydrogenation. This activation phenomenon accounts for the induction periods noted during many hydrogenation runs. The induction periods in the present investigation were relatively short when the newer catalysts were used. Apparently these catalysts were already almost completely activated to the highest degree possible commensurate with their available surface area and the character of that area.

The method of treating and the material used to treat nickel catalysts obviously can induce large changes in the overall performance of the catalyst. Zajcew (16) has also changed selectivity and isomerization, but he had used bismuth and silver to deactivate partially a palladium catalyst. Additional research is recommended in an attempt to link the structural and chemical properties of the catalyst with its performance characteristics during hydrogenation.

The present results offer an important lead for the development of new catalysts which could be used for the production of new types of hydrogenated products. Hydrogenated products with significantly different selectivity ratios or degrees of isomerization possibly have physical, chemical or nutritional properties which are or will be of interest. Modified or treated catalysts may be the key to the production of such products.

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