A New Process for the Selective Hydrogenation of Cyclopropenoids in Cottonseed Oil

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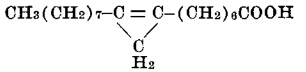
Abstract

A new process has been developed, in which the cyclopropenoid groups in cottonseed oil can be selectively and continuously hydrogenated under mild conditions. This process utilizes nickel in a fixed-bed reactor, thereby eliminating the expensive filtration commonly associated with slurry reactors.

In pilot-plant runs at essentially atmospheric pressure and at temperatures from 150 to 315F (66–157C), Halphen-negative oils were produced in as short a contact time as 2 min. Little or no hydrogenation or isomerization of normal fatty acids occurred during the process. Reaction rate data indicate that cyclopropenoid removal follows first-order behavior.

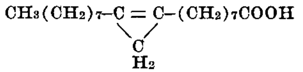
Introduction

One of the minor ingredients of cottonseed oil is a class of fatty acid compounds containing a cyclopropenoid group, thought to be chiefly malvalic and sterculic acid.



$\mathrm{CH_3(CH_2)_7{-}\underset{\diagdown\ \diagup \atop {C \atop H_2}}{C{=}C}{-}(CH_2)_6COOH}$

Malvalic Acid



$\mathrm{CH_3(CH_2)_7{-}\underset{\diagdown\ \diagup \atop {C \atop H_2}}{C{=}C}{-}(CH_2)_7COOH}$

Sterculic Acid

They are reported to promote adverse biological effects in chickens (5). The most common effect has been to enhance the red discoloration of egg whites. Other effects have been reported; these have been reviewed by Phelps et al. (4).

These cyclopropenoid groups can be inactivated by hydrogenating the cottonseed oil. Merker and Mattil have shown that the cyclopropenoid groups can be selectively hydrogenated with nickel, platinum, and palladium catalysts at high temperatures in slurry reactors (3). More recently Ward et al. (6) reported the selective hydrogenation of cyclopropenoids in batch slurry reactors by using nickel catalysts under mild conditions. Their process however required moderately long reaction times and was not completely selective. Significant reductions in the iodine value accompanied cyclopropenoid hydrogenation.

The present study describes a technique for selectively hydrogenating the cyclopropenoid groups in a packed-bed reactor by using nickel catalysts at mild temperatures, atmospheric pressure, and short reaction time.

Experimental Procedures

Cottonseed oil (previously refined and bleached) containing 0.72 wt % cyclopropenoids was hydrogenated in a packed-bed reactor. This reactor, operated in a batch, total-recycle manner, is illustrated in Fig. 1. The reactor itself consisted of a 2-ft length of 1½-in. Schedule 40 stainless steel pipe. All other parts of the equipment that contacted the oil were of stainless steel. Stainless steel wire screen (about 200 mesh), placed in the bottom of the reactor, supported the catalyst bed.

Two fixed-bed nickel catalysts were tested: a commercial catalyst (Girdler G-52), a prereduced stable catalyst in the form of ¼-in. long × ¼-in. diameter cylinders, containing 33% nickel; and an experimental catalyst containing about 12.5% nickel in irregular particles in the 8/10 mesh-size range. Nickel catalysts were selected on the basis of preliminary catalyst-screening in conventional, stirred-batch slurry reactors. Nickel was found to be the only type of catalyst that would selectively hydrogenate the cyclopropenoids without reducing the fatty acid unsaturation; platinum, palladium, rhodium, and ruthenium reduced the total unsaturation of the oil considerably (5–30 iodine value units) during cyclopropenoid removal.

An oil charge of either 2,500 or 3,000 g was used in all runs; the catalyst charge was either 670 g (G-52) or 910 g (experimental). The reactor was filled with catalyst; because of density differences, different amounts of catalyst were used. Both catalysts were treated with flowing hydrogen at 750F for 3 hr in the reactor prior to admitting oil to the system. Three reaction temperatures were studied; 150, 250, and 315F. Temperature was measured at the reactor outlet with a thermometer; since reaction heat effects and reactor heat losses were negligible, these temperatures represented the average temperature in the catalyst bed. Pressure was not varied; the inlet pressure was 10 psig and the outlet pressure was substantially atmospheric.

After the catalyst was reduced and cooled to room temperature (under a nitrogen atmosphere), the oil was charged and recirculated through the system, while nitrogen was passed through the reactor, until the desired operating temperature was obtained. Hydrogen was then substituted for nitrogen, and small samples were withdrawn at regular intervals of time.

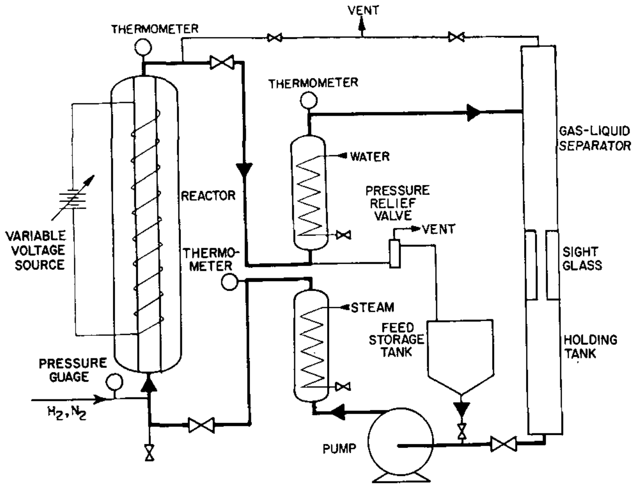


Fig. 1. Packed-bed reactor.

Superficial velocities of the oil through the catalyst bed (pump-discharge rate divided by the empty reactor cross-sectional area) were normally maintained at 0.26 ft/sec. At this velocity all of the oil in the system was recycled in about 30 sec. The relative unimportance of thermal hydrogenation (noncatalytic) was confirmed by runs in which no catalyst was used. Although a slow disappearance of cyclopropenoids occurred, it was several orders of magnitude slower than the catalytic hydrogenation rates.

Analysis of the cyclopropenoid content was made by the stepwise HBr addition technique described by Harris et al. (1,2). Fatty acid composition of the oil was determined after esterification (acid-catalyzed transesterification) by gas chromatography, *trans* bonds by infrared spectroscopy, and total unsaturation by iodine absorption (iodine value).

Results and Discussion

Product Properties

Both of the nickel catalysts that were tested exhibited high selectivity for hydrogenation of the cyclopropenoid bonds with little accompanying hydrogenation of the normal fatty acid unsaturation. Table I shows the properties of cottonseed oil which has been hydrogenated at several different temperatures with the commercial and the experimental nickel catalysts. There is no significant change in the iodine value, *trans* isomer content, or fatty acid composition for any of the runs; as much as 98.6% of the cyclopropenoids has been inactivated. Thus selectivity is not a function of temperature over the range of 155–315F. This high selectivity should also hold at even higher temperatures. By increasing the reaction temperature, the reaction rate is increased, and much shorter reaction times are needed to reduce the cyclopropenoids to a given concentration.

The data in Table I represent an arbitrary cut-off point in sampling during each of the runs. With sufficient time, the cyclopropenoid concentration could be reduced to approximately zero under any of the temperatures studied. Approximate contact time refers to the estimated amount of time the oil spent in the catalyst bed itself; it is calculated by multiplying the total elapsed run-time by the fraction of the total oil in the system that was held in the catalyst bed. For example, for the first run (155F commercial catalyst), the total elapsed run-time was 30 min. The weight of the total oil charge estimated to be in the reactor bed (based on a void fraction in the bed of 0.32) was 225 g. The estimated contact times would then be 30 × 225/2500 or 2.7 min. Cyclopropenoid concentration is calculated as wt % of sterculic acid.

One question that might be raised is "what degree of cyclopropenoid removal is desirable?" A possible answer is sufficient hydrogenation to lower the cyclopropenoids concentration to the point that the oil gives a negative response to the Halphen test. Cottonseed oils which were Halphen-negative do not exhibit the harmful effects on chicken eggs that Halphen-positive oils do (4). In the present study Halphen-negative oil corresponds to a cyclopropenoid concentration of approximately 0.01 wt %. Thus Halphen-negative cottonseed oil can be made in a fixed bed of nickel catalyst, under mild conditions, with contact times of 2 min or less. Such an oil would possess essentially the same composition as the unhydrogenated oil except for the lowered cyclopropenoid level.

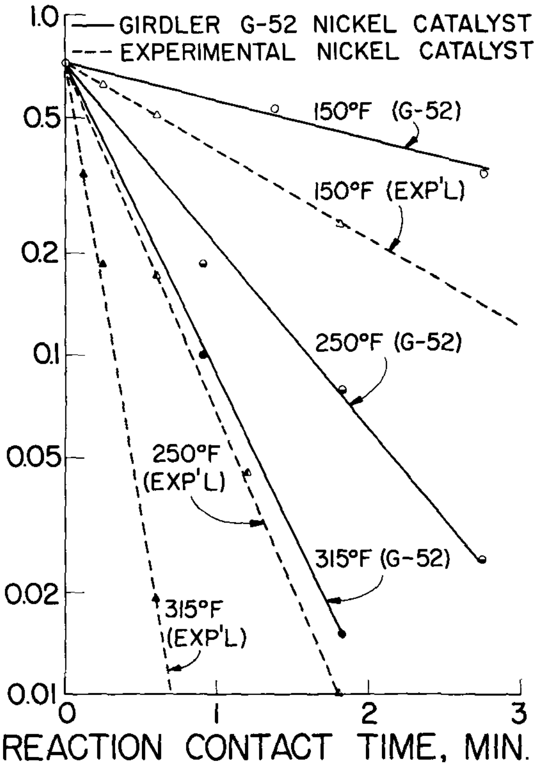


FIG. 2. First-order dependence of reaction rate on cyclopropenoid concentration.

Reaction Kinetics

Cyclopropenoid disappearance appears to follow the first-order rate equation

$$\frac{-d\, C_{cp}}{dt} = k\, C_{cp} \qquad [1]$$

where C_{cp} = concentration of cyclopropenoids in the bulk oil, wt %

t = time, minutes

k = rate constant, minutes^{-1}

TABLE I

Selective Hydrogenation Results

Temperature °F	Catalyst	Catalyst (g)	Oil (g)	Approximate contact time, min	Cyclopropenoids wt %	Iodine value	*trans* Bonds wt %	Gas Chromatographic Analysis wt % Palmitic	Stearic	Oleic	Linoleic
Starting oil	....			....	0.72	110.5	0	23.8	2.4	17.5	54.3
155	Commercial[a]	670	3000	2.7	0.33	111.5	0.9	24.1	2.1	17.4	55.1
155	Experimental	905	2500	3.6	0.084	109.5	...	24.3	2.4	17.9	54.1
250	Commercial[a]	670	2500	2.7	0.025	111.0	1.1	24.2	2.1	17.3	55.1
250	Experimental	910	2500	1.8	0.010	111.0	....	......	....	.....	......
315	Commercial[a]	670	2500	1.8	0.015	110.0	....	23.8	2.4	18.3	53.3
315	Experimental	910	2500	0.6	0.019	111.5	....	......	....	......	......

[a] Girdler G-52.

The reaction would also be a function of the hydrogen concentration at the catalyst surface but, since the pressure was held constant at about 10 psig, the hydrogen concentration in the oil would remain constant. (Excess hydrogen was used in all runs; it may thus be assumed that the concentration of hydrogen dissolved in the oil was equilibrium concentration for 10 psig and the particular reaction temperature.)

This first-order dependence of reaction rate on cyclopropenoid concentration is illustrated in Fig. 2. The log of the concentration of cyclopropenoids is plotted versus time to give straight lines, a standard technique for establishing first-order behavior. The data present only the nature of the reaction order and the temperature dependency for each catalyst. Since the two catalysts did not have the same amount of external surface area and the relative amounts of catalyst and oil were not the same in each run (Table I), the relative activity of the two catalysts cannot be compared in this plot.

Catalyst Life

How rapidly does the activity of the catalyst decline during hydrogenation? Obviously this process depends on having a fairly stable catalyst. The approximate extent of commercial catalyst deactivation with continued use was obtained by hydrogenating successive batches of oil with the same catalyst charge. At the end of 71 runs at 250F, 15 psig inlet pressure (outlet pressure, 0 psig), and 15-min duration, in which the cyclopropenoid content was reduced to approximately 0.15 wt %, the commercial catalyst had only lost 8.5% of its initial activity. Over this period 265 g of oil had been hydrogenated per gram of catalyst. The charge oil was exposed to the atmosphere and probably contained equilibrium amounts of oxygen and water. Since these two contaminants are believed to deactivate hydrogenation catalysts in general, a large portion of the decline should be prevented by simple nitrogen stripping of the oil.

Although not directly connected with activity, one potential disadvantage in regard to catalyst life should be mentioned. With the specific batch of G-52 catalyst that was used during this study, a gradual attrition occurred, giving a dilute suspension of fine particles in the oil. Whether this attrition loss is typical of the catalyst or whether this eventually will diminish was not explored. No appreciable attrition was observed with the experimental catalyst, but it is safe to speculate that a polish filtration step would remove any that did occur.

Economics

It is estimated that the total cost of such a fixed-bed hydrogenation process for removing cyclopropenoids from cottonseed oil ($\leqslant$0.01% in product) would be from 0.13 to 0.25 cents/lb of oil processed. (These numbers are based on fixed-bed hydrogenation experience at Procter and Gamble.) The exact value would depend on the catalyst life. For example, for a life equivalent to 6,000 lb of oil processed per pound of catalyst, catalyst costs would be approximately 0.05 cents/lb of oil if a catalyst cost of $3/lb is assumed.

By using the contact times shown in Fig. 2 as a basis for scale-up, a reactor design for producing Halphen-negative cottonseed oil at a rate of 10,000 lb/hr was estimated. Such a reactor, containing commercial catalyst and operating at 315F and 10 psig inlet pressure (outlet pressure was 0 psig), requires a catalyst volume of 12.9 cu. ft. For a superficial oil flow rate of 0.10 ft/sec (slowing the superficial velocity from 0.26 to 0.10 ft/sec was found experimentally to increase the reaction time by only 10%), the corresponding reactor dimensions would be 10 in. in diameter, 24 ft in length. These calculations assume that the catalyst life will be reduced by 50% after 60,000 lbs of oil have been hydrogenated per pound of catalyst. This reactor then will be over-designed by a factor of 2. No additional hydrogenation of the fatty acid groups of the oil should result in the initial period of operation. The only effect would be lowering of the cyclopropenoid content below 0.01% during the initial phase.

In summary, it was shown that a fixed bed of nickel catalyst can be used at 10 psig, 250–315F to hydrogenate selectively the cyclopropenoid groups of cottonseed oil. Such a process appears to be relatively inexpensive and practical. Although only two different nickel catalysts were examined, the selectivity results are probably valid for any type of nickel catalyst. Activity and catalyst life must be measured on the specific catalyst chosen for use.

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