Catalytic Elimination of Cyclopropene-Containing Acids[1]

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Abstract

A procedure is described for decreasing the cyclopropene ring acids in cottonseed oil triglycerides as indicated by the Halphen test. Continuous reaction of the oil in the presence of aluminum silicate catalyst at elevated temp effectively decreases its cyclopropene acid content. The effect of temp and space velocity are described from temp of 170–225C. The treated oil produces no observable effect on egg quality or production.

Introduction

It has been established that two of the acids in the triglycerides of cottonseed oil contain a cyclopropene ring and give the Halphen test (7,8). If these acids (sterculic or malvalic) are fed to laying hens in sufficient concentrations, the whites of the eggs turn pink (3) and the embryos of fertilized eggs show essentially 100% mortality (6).

If it becomes apparent, at some time in the future, that the elimination of these components from cottonseed oil is necessary, it would be desirable to have some method available.

A system for elimination of the cyclopropene ring should have no adverse effects on the other fatty acids present in the oil. Previous work has indicated that hydrogen chloride, sulphur dioxide (2), and sulphur dioxide adsorbed on aluminum oxide (5) destroys the cyclopropene configuration.

This study presents a process whereby the cyclopropene content was reduced by the passage of cottonseed oil over a fixed bed catalyst. Based upon the evaluations made, a commercially usable oil might be produced under selected operating conditions.

Experimental

Two procedures were followed in conducting the experiments. In the first, a number of catalysts were screened in a batch process. Those that were found active were then subjected to additional testing in a continuous apparatus.

The batch procedures were carried out as follows: A 300-cc round bottom, three-necked flask equipped with a stirrer, thermometer, condenser, and gas inlet tube, and heated by an oil bath was charged with 2.5 g catalyst and 25 ml refined bleached and deodorized cottonseed oil. A nitrogen atmosphere was maintained in the flask. Initially a number of petroleum cracking catalysts were examined at 180 ± 3C and finally the more active materials at 130 ± 3C. The reaction time was 2 hr after which the oil was cooled and centrifuged. The concentration of Halphen acids was determined before and after treatment.

In the continuous procedure a Hills-McCanna proportionating pump, Model #UN2F with a micrometer variable ¼-in. diam piston was used to pump cottonseed oil through a Kuntzel reactor charged with the catalyst. The reactor, manufactured by Autoclave Engineers, had an overall length of 18 in., a 2 in. outside diam and a 1 in. inside diam. It was warmed with Nichrome resistance wire of an approximate heating capacity of 500 w. The reactor was immersed in a 6 in. diam oil bath. A stirrer provided the necessary agitation for temp uniformity. It was found that for more rapid heat-up a 250 w auxilary immersion heater was desirable. The entire system was controlled to ± 2C by a silicon controlled rectifier system (Dynapac 20, Labline). The oil flow proceeded from a reservoir to the pump, through the reactor charged with catalyst, a cooling coil, and, finally, into a receiver. The temp and pumping rate were varied to determine the optimum conditions of operation.

The quantities of cyclopropene fatty acids in the oils were estimated by the Halphen test (1), the free fatty acids by AOCS Method No. Ca 5a-40 (4), the iodine number by AOCS Method No. Cd 1-25 (4), and conjugated dienes by UV spectroscopy. A molar extinction coefficient of 27,000 was used with an equivalent wt of 294. The amount of water in the oil was determined by the Karl Fischer method.

Results

Results from the batch-scale screening experiments given in Table I indicated that Nalcat and DA-1 were the most active of the catalysts used.

The two best catalysts obtained as a result of the batch screening were tested in the continuous system described. The results of these tests are given in Table II. The Nalcat catalyst seemed to have a slightly higher degree of activity than DA-1 and was chosen for subsequent studies.

TABLE I

Batch Treatment of Refined, Bleached, Winterized Cottonseed Oil to Reduce Halphen Acid Content

Catalyst	Temp C ± 3°	Halphen Acid (1) % wt
Control (no catalyst)	180	0.31
Nalcat high alumina-silica (More acidic than filtrol 100. Nalco Chem. Co.)	180	0.00
Filtrol 100 silica-alumina (Prepared from the natural mineral; more acidic than Englehard. Sinclair Res. Inc.)	180	0.06
Englehard alumina (High surface area; more acidic than Nalco. Englehard Ind.)	180	0.19
Nalco alumina (High surface area; acidic; Nalco Chem. Co.)	180	0.02
DA-1 (Cracking catalyst. 13% alumina and 8% silica. Small number of highly acidic sites. Esso Res. & Eng. Co.)	180	0.00
3E (Cracking catalyst. 35% magnesia and 65% silica. Large number of low acidity sites. Esso Res. & Eng. Co.)	180	0.27
Alcoholate alumina (Essentially no acidic sites. Esso Res. & Eng. Co.)	180	0.27
Control (no catalyst)	130	0.31
Filtrol 100	130	0.19
Nalco	130	0.29
Nalcat	130	0.11
DA-1	130	0.04

TABLE II

Continuous Treatment of Refined, Bleached, Winterized Cottonseed Oil to Reduce Halphen Acid Content

Catalyst	Temp C ± 3°	Ml oil/g cata./min	Halphen acid (1) % wt
Nalcat	180	0.159	0.00
	130	0.156	0.13
DA-1	180	0.168	0.07
	130	0.181	0.24

[1] Work carried out under grant from Hunt Foods Industries, Inc.

TABLE III

Effects of Temperature and Space Velocity in the Continuous Treatment of Refined Cottonseed Oil with Nalcat Catalyst

Temp C ± 3°	Ml oil/g cata./min	Halphen acid (1) % wt	Free fatty acids % wt	Conjugated diene % wt	Iodine no.
Untreated oil		0.70	0.07	0.28	112.5
170	0.034	0.04	3.40	1.70	109.0
170	0.050	0.10	2.80	1.30	108.0
170	0.072	0.17	2.30	1.20	102.0
180	0.052	0.09	3.20	1.70	109.0
180	0.097	0.18	2.80	1.30	109.0
180	0.148	0.30	1.90	0.90	108.0
190	0.104	0.15	3.10	1.40	110.0
190	0.149	0.19	3.00	1.10	110.0
190	0.200	0.30	2.40	0.80	110.0
225	0.050	0.01	24.70	6.70	103.2
225	0.149	0.01	12.50	4.50	107.9
225	0.221	0.05	3.30	3.60	110.7
225	0.353	0.16	1.80	1.80	111.9

Sample #62-1944 Nalcat (manufactured by Nalco Chemical Co.) reportedly had on a dry basis 2.2% volatile material at 1800F, 24.4% Al_2O_3, 0.038% Na_2O, 0.25% SO_4, and 0.035% Fe. Also, the sample was described as having:

Surface area: 370 m^2/g
Pore volume: 1.08 cm^3/g
Pore diam: 117 Å
Apparent bulk density: 0.39 g/cc
Strength: 9.5 lb to crush
⅛ in. diam by ¼ in. long extrudate

Sterculia foetida oil, which contains about 50% cyclopropene acids as triglycerides (7), was diluted with an equal volume of corn oil and treated by the batch process with the Nalcat catalyst at 180C. After 21 hr the Halphen test was negative.

Two groups of laying hens were fed a basal corn-soy diet (2) to which was added the equivalent of 50 mg treated and 50 mg untreated methyl sterculate daily for 10 days. The hens fed the diet containing untreated oil stopped laying toward the end of the testing period. Those fed the diet containing treated oil continued to lay without any observable change in production.

The eggs were collected, stored for a period of 5–6 weeks and examined. A total of 79.5% of the production from 5 hens fed untreated *Sterculia foetida* oil had yolks with the consistency of putty and the albumin was slightly pink. Hens that had received the treated *Sterculia foetida* oil yielded normal eggs.

Three groups of day-old chicks were fed a basal corn-soy diet (2), the basal diet supplemented with the equivalent of 66 mg/lb methyl sterculate as *Sterculia foetida* oil or with the equivalent of 66 mg/lb methyl sterculate as treated *Sterculia foetida* oil. No significant differences in mortality or wt gains were attributable to either of the *Sterculia foetida* oil groups when compared to the control group.

Continuous treatments were carried out on cottonseed oil that had been dried but not bleached or deodorized, commercial cottonseed oil that is available in the average retail store, and finally, refined cottonseed oil that had been deliberately saturated with water.

Table III shows the effect of different space velocities on the Halphen content, free fatty acids, iodine number, and percent conjugation at 170,180,190, and 225C. Oil that had been completely refined and dried except for deodorizing and decolorizing was used for these studies.

Refined commercial cottonseed oil, obtained from a retail grocery market, was treated continuously at

TABLE IV

Effect of Water on Continuous Treatment of Bleached, Winterized, Refined Cottonseed Oil with Nalcat Catalyst

	Water % wt	Free fatty acids % wt	Halphen acid (1) % wt
Commercial oil Untreated	0.04	0.04	0.31
Commercial oil Treated	......	1.70	0.04
Commercial oil Sat. with H_2O [a] Untreated	0.14	0.04	0.31
Commercial oil Sat. with H_2O [a] Treated	......	4.70	0.00

[a] Saturated by shaking with excess H_2O for 2 hr and allowed to clear by settling.

180C. The results are indicated in Table IV. A sample of the same oil was saturated with water and passed continuously through the fixed bed system. The results are also shown in Table IV.

Discussion

Examination of Table III shows the effect of temp and the space velocity, which is inversely proportional to reaction time, upon the changes induced in cottonseed oil by the catalyst. Increased temp permit much shorter reaction times for decreasing the Halphen acids. Too great a reaction time at any temp brings about the formation of large amounts of free fatty acids accompanied by an increase of conjugated dienes. At any one temp a space velocity can be found that yields a low Halphen acid content with limited amounts of free fatty acids and conjugated dienes being formed. If the reaction conditions are not too drastic, the iodine number of the oil remains essentially unchanged.

Table IV indicates that for practical application of the catalyst in the reduction of cyclopropene acids, water must be removed from the oil. If high concn of water are present, the formation of free fatty acids is markedly increased thus resulting in high refining losses.

The data indicate that under selected reaction conditions the cyclopropene content of cottonseed oil can be decreased and that a refinable oil can be produced by an aluminum silicate catalyst.

The resultant oil obtained when this catalyst was used had no observed adverse effects when fed to chicks and laying hens. Concn of cyclopropene-containing acids in oils sufficiently high to bring about a 79.5% discoloration in stored eggs after treatment with the catalyst produced no observable effect on the eggs nor the production of the laying hens.

The increase in conjugate unsaturation probably arises from two sources, opening of the cyclopropene ring and isomerization of non-conjugated to conjugated fatty acids. These products do not appear to have any harmful effects as judged by the limited feeding studies that have been conducted.

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