Elimination of the Halphen Response of Cottonseed Oils in Conjunction with Deodorization[1]

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Abstract

Two simple but effective pilot-plant processes were developed to produce Halphen-negative cottonseed oil. Both involve treatment of the oil with cottonseed fatty acids in a conventional batch type of deodorizer in conjunction with deodorization. In one process, in which the acids were added to the oil, the cyclopropenoids were inactivated in as short a time as 5 min after the oil reached the maximum temperature of 450–455F. In the other, in which the acids were generated in situ, the oil did not become Halphen-negative until about an hour and 45 min after it reached maximum temperature. The excess acids produced by both methods were readily removed during conventional deodorization. In contrast, deodorization alone reduced the cyclopropenoid content of the oil to a low level (0.02%) but did not render it Halphen-negative even after 3 hr at maximum temperature.

These new processes are directly applicable for use by refineries that have the batch type of deodorizers. For refineries that operate continuous or semicontinuous deodorizers, it should be relatively simple to design preheating vessels or heat exchangers to inactivate partially or completely the cyclopropenoids before deodorization.

Introduction

MANY OILSEEDS, including cottonseed, contain cyclopropenoid acids (malvalic and sterculic) in their triglycerides (1,2). Although the concentration of cyclopropenoids in cottonseed oil is relatively small (3–6), the incorporation of low levels of cottonseed oil containing cyclopropenoids and giving a positive Halphen reaction into the diet of laying hens results in unusual biological effects, such as production of eggs with pink whites; decreased pH of whites; increased pH of yolks; enlarged, mottled yolks upon storage (1,2); and lower ratios of oleic acid to stearic acid in yolk lipids or tissue lipids (7–10). Fortunately, if the cyclopenoids are inactivated before being ingested by laying hens, the biological effects are no longer observed (10–12).

As far as is known, no adverse effects have been attributed to consumption of cottonseed oil by human beings. Nevertheless the cottonseed industry has become interested in the development of an economical method of producing cottonseed oil essentially free of cyclopropenoids.

Based on a laboratory procedure reported earlier (12), two simple pilot-plant processes were developed to eliminate the cyclopropenoids, as evidenced by a negative Halphen response, in refined and bleached cottonseed oils by treatment with cottonseed fatty acids in a batch type of deodorizer in conjunction with deodorization. For comparison, the degree of inactivation by conventional deodorization alone was also investigated.

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Materials and Equipment

The oil used for all experiments was a commercial, refined, bleached, winterized, Halphen-positive cottonseed oil, which had not been deodorized, containing about 0.53% cyclopropenoids and 0.06% free fatty acids. Oil that has not been winterized can also be used. The redistilled fatty acids were an Emery Industries product designated as number 600, cottonseed type of fatty acids.

A batch-type, stainless-steel, pilot-plant deodorizer vessel with a capacity for about 350 lb of oil was used (13). It is similar to the large-batch deodorizers used in many refineries with several exceptions. It has a removable cover to permit the interior to be inspected and cleaned. The vapor take-off is connected to the side near the top. It is equipped with external heating coils above the oil level to minimize condensation of volatile material. The lower quarter of the vessel is equipped with a double bank of internal coils and a baffled jacket.

Heating or cooling was achieved by forced circulation of Therminol heat-transfer liquid through the coils and jacket of the vessel. The Therminol was heated with electrically heated exchangers and cooled by a high capacity water-cooled exchanger. The system was equipped with a by-pass loop in which the Therminol was preheated before it was admitted to the heating coils and jacket of the vessel.

Sparging steam at 30 psi supply pressure was introduced via a 16-in-diameter single coil, perforated steam distributor, located about 3 in. above the bottom of the vessel, with the perforations directed downward. Sparge-steam flow-rate was controlled with an insulated steam flowmeter.

A triple-stage steam ejector system was used to reduce the pressure in the deodorizer. For a vacuum of about 17–19 in. Hg, only the third stage of the ejector was used, and the vacuum was regulated by throttling the steam flow through the ejector. When a vacuum of 29.8 in. Hg was desired, the three stages of the ejector were used with maximum flow.

A horizontal plate filter connected to the bottom outlet of the vessel was used to filter and polish the processed oil.

Procedures

In one of the pilot-plant processes the required cottonseed fatty acids were added to the oil at one of three levels: 1.6, 1.0, or 0.4 equivalents, based on the cyclopropenoid content of the oil. In the other, they were generated in situ. With this exception the experimental procedures were the same for both processes.

The Therminol in the heat-transfer system was circulated through the by-pass loop and heated to about 545F before the oil was introduced into the deodorizer. The deodorizer was then placed under about 17–19 in. Hg vacuum, and the appropriate sample—cottonseed oil and cottonseed acids in the first process, cottonseed oil alone in the second process—was charged into the deodorizer by suction.

The hot Therminol was then admitted into the internal heating coils and jacket of the deodorizer vessel, and the by-pass loop of the heat transfer system was closed. After the hot fluid had circulated for about 25 min, steam sparge of about 1–2 lb of steam per hr per 100 lb of oil was injected through the steam distributor. Within 3½ hr the temperature of the oil had increased to 450–455F and was thereafter held constant.

Samples were collected at 30-min intervals and immediately tested for Halphen response and for free-fatty acid content (14), calculated as oleic acid. Selected samples were later analyzed for cyclopropenoid content, determined by the HBr titration technique (6) and calculated as malvalic acid.

After the response to the Halphen test became negative, the vacuum was increased to 29.8 in. Hg and the steam sparge to about 3–5 lb of steam per hour per 100 lb of oil to distill off the excess free-fatty acids and deodorize the oil. After deodorization, the oil was cooled under vacuum to about 150F as rapidly as possible and then allowed to cool further over-night under a blanket of nitrogen. It was then filtered and stored in a drum.

Results

Elimination of Halphen Response

Treatment with Added Cottonseed Acids. Table I shows the results obtained when 1.6 equivalents of cottonseed fatty acids were added to the oil. It should be noted that the time recorded for each procedure is the maximum needed to eliminate the Halphen response since the oil could have become negative at any time within the half-hour sampling interval. With 1.6 equivalents, for example, the first sample giving a negative response was withdrawn 5 min after the oil had reached the maximum temperature of 450–455F; conversion could have occurred however any time after the previous sample was taken. In this case, since the response at 445F was just barely positive, the oil probably became negative before maximum temperature was attained.

The data in Table I suggest that inactivation of the cyclopropenoids proceeded as follows. During the major portion of the heat-up period, the consumption of free-fatty acids by the reaction of their carboxyl group with the cyclopropenoid moiety was greater than the production of free-fatty acids by fat splitting; the net result was a gradual decrease in the concentration of acids from 0.86% to 0.64%, together with a simultaneous, rapid decrease in the concentration of cyclopropenoids. After most of the cyclopropenoids had been inactivated the production of free-fatty acids exceeded their consumption so that there was a net increase in acidity to 0.89%, a concentration more than sufficient to inactivate the remaining trace amounts of cyclopropenoids. These observations agree with previous findings (15,16) on the acetolysis or cleavage of the cyclopropenoid moiety by the carboxyl group of the free-fatty acids and also with results (17) on fat splitting at high temperature in the presence of a steam sparge. The excess acids were then readily removed by increasing the vacuum to 29.8 in. Hg.

Similarly, when 1.0 equivalent of cottonseed acids was employed, there was a gradual decrease in the concentration of cottonseed acids from 0.50% to 0.34% during the major portion of the heat-up period, followed by a gradual increase to 0.68% during the remainder of the high-temperature treatment under low vacuum. Again, there was a rapid decrease in the concentration of cyclopropenoids, but in this case the oil did not become Halphen-negative until it had been heated at 450–455F for 25 min.

For the addition of 0.4 equivalent, the corresponding figures for the concentration of cottonseed acids were an early decrease from 0.23% to 0.18% and then a gradual increase to 0.50%. It took an hour and 15 min at 450–455F to render the oil Halphen-negative in contrast to about 5 min with 1.6 equivalents and 25 min with 1.0 equivalent.

Treatment with Generated Cottonseed Acids. These observations suggested that it might be possible to inactivate the cyclopropenoids by generating the required cottonseed acids in situ. As shown in Table II, acids generated by the steam sparge were almost as effective as added acids in reducing the concentration of cyclopropenoids to a level of about 0.04%. Beyond this point the in situ procedure took an hour and 45 min at 450–455F to render the oil Halphen-negative, a longer time than any of the processes in which cottonseed acids were added.

Partial Inactivation of Cyclopropenoids

The inactivation of cyclopropenoids under conditions simulating those used during commercial deodorization was also investigated. Like the pilot-plant procedures, deodorization involves heating the oil in the presence of a steam sparge, but it differs from these processes in that higher vacuum is maintained throughout—29.8 in. Hg instead of the 17–19 in. Hg initially used in the pilot plant.

Comparison of Tables II and III shows that during most of the heat-up period the decrease in the con-

TABLE I

Elimination of Halphen Response in Cottonseed Oil by Treatment with Added Cottonseed Fatty Acids (1.6 Equivalents)

Time[a] (hr)	Temperature (F)	Vacuum (in. Hg)	Halphen response	Cyclopropenoids (%)	Acidity (%)
0.0	95	19	+	0.53	0.86
0.5	130	19	+	.....	0.85
1.0	325	19	+	0.38	0.81
1.5	375	19	+	.....	0.75
2.0	405	18	+	0.03	0.68
2.5	430	17	+	.....	0.64
3.0	445	15	+[b]	0.01[c]	0.72
3.5	452	17	—	0.01[c]	0.79
4.0	453	17	—	.....	0.89
4.5	438	29.8	—	.....	0.05
5.0	445	29.8	—	.....	0.03
5.5	447	29.8	—	0.01[c]	0.02
7.5	160	0.0	—	.....	.....

[a] Time elapsed after injection of steam sparge.
[b] Response only slightly positive, if at all.
[c] Within sensitivity limits of the method.

TABLE II

Elimination of Halphen Response in Cottonseed Oil by Treatment with Cottonseed Fatty Acids Generated in situ

Time[a] (hr)	Temperature (F)	Vacuum (in. Hg)	Halphen response	Cyclopropenoids (%)	Acidity (%)
0.0	90	12	+	0.53	0.06
0.5	103	12	+	.....	.....
1.0	300	11	+	0.49	0.06
1.5	350	18	+	.....	0.03
2.0	388	18	+	0.04	0.02
2.5	415	18	+	.....	0.03
3.0	438	18	+	0.03	0.06
3.5	455	18	+	.....	0.10
4.0	454	18	+	0.02	0.15
4.5	455	18	+	.....	0.20
5.0	455	18	+	0.02	0.28
5.5	442	29.8	—	.....	0.03
6.0	454	29.8	—	.....	0.02
6.5	456	29.8	—	0.01[b]	0.01
8.5	157	0.0	—	.....	.....

[a] Time elapsed after injection of steam sparge.
[b] Within sensitivity limits of the method.

TABLE III

Partial Inactivation of Cyclopropenoids in Cottonseed Oil by Conventional Deodorization

Time[a] (hr)	Temperature (F)	Vacuum (in. Hg)	Halphen response	Cyclopropenoids (%)	Acidity (%)
0.0	95	29.8	+	0.53	0.06
0.5	330	29.8	+	.....	
1.0	360	29.8	+	.....	0.04
1.5	390	29.8	+	0.24	0.02
2.0	430	29.8	+	.....	0.02
2.5	450	29.8	+	0.04	0.02
3.0	452	29.8	+	.....	.....
3.5	452	29.8	+	0.03	0.02
4.0	453	29.8	+	.....	0.02
4.5	455	29.8	+	0.02	0.01
5.0	453	29.8	+	.....	0.01
5.5	455	29.8	+	0.02	0.01
7.5	130	0.0	+	0.02	0.01

[a] Time elapsed after injection of steam sparge.

centration of cottonseed acid is similar for both the in-situ process and conventional deodorization, accompanied in each case by a reduction in cyclopropenoids to a low level. As the temperature approached maximum, the concentration of acids increased enough under the low vacuum used in the in-situ process (no acids were distilled off) to inactivate the remaining cyclopropenoids. In conventional deodorization the acids generated at high temperature were distilled off too rapidly to react completely with these trace amounts. Thus, although the level of cyclopropenoids was reduced from 0.53% to 0.04% when maximum temperature of 450–455F under high vacuum was attained, then to 0.02% after 3 hr at this temperature, the oil was not rendered Halphen-negative as it was in the other procedures.

Discussion

An unexpected dividend in scaling-up the laboratory procedure (12) for the preparation of Halphen-negative cottonseed oils by heat treatment in the presence of cottonseed acids was that the pilot-plant process proved to be considerably more efficient than the laboratory process. The steam sparge and the greater depth of the oil in the pilot-plant deodorizer provided more vigorous agitation and better contact between the oil and the free fatty acids than was provided by the nitrogen sparge and the shallow depth of the oil in the laboratory deodorizer. Furthermore the steam sparge promoted fat splitting, which resulted in the availability of an additional small amount of freshly cleaved cottonseed acids to inactivate the cyclopropenoids. It is also believed that the presence of moisture tended to promote the reaction. Thus, in the laboratory, refined and bleached cottonseed oil containing about 0.53% cyclopropenoids had to be heated for 2 hr at 450–455F, in the presence of four equivalents of cottonseed acids, to be rendered Halphen-negative. In the pilot plant however the same level of cyclopropenoids was inactivated with 1.6 equivalents of added acids within minutes after the maximum temperature was reached.

In the special processes developed for the elimination or reduction of the Halphen response in cottonseed oil, the reaction products formed by the cyclopropenoids of cottonseed oil in the presence of cottonseed acids have not been isolated and characterized. These products however should be similar to the ones found in deodorized cottonseed oils since cottonseed acids are normally present or generated in situ during conventional deodorization. The iodine value, peroxide value, and AOM stability of these specially processed cottonseed oils were comparable with similar values of cottonseed oils processed by the conventional batch type of deodorization. These observations suggest that the special treatments in conjunction with deodorization do not have any detectable adverse effects on the physical properties of the oil. Also, preliminary studies indicated that the losses encountered during these special treatments can be kept to less than 1%.

Limited biological studies of oils similarly processed on a laboratory scale showed that they did not produce any unusual physiological effects (12), but extensive biological studies of the oils prepared in the pilot plant are now in progress.

These experiments indicate that, if the need should arise, refineries which use the batch type of deodorizers could readily render refined and bleached cottonseed oils Halphen-negative or reduce the concentration of cyclopropenoids to low levels, as desired. Although the processes described are not directly applicable to refineries using continuous or semicontinuous deodorizers, it should be relatively simple to design preheating vessels or heat exchangers for the partial or complete inactivation of the cyclopropenoids before the oil enters the deodorizer.

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