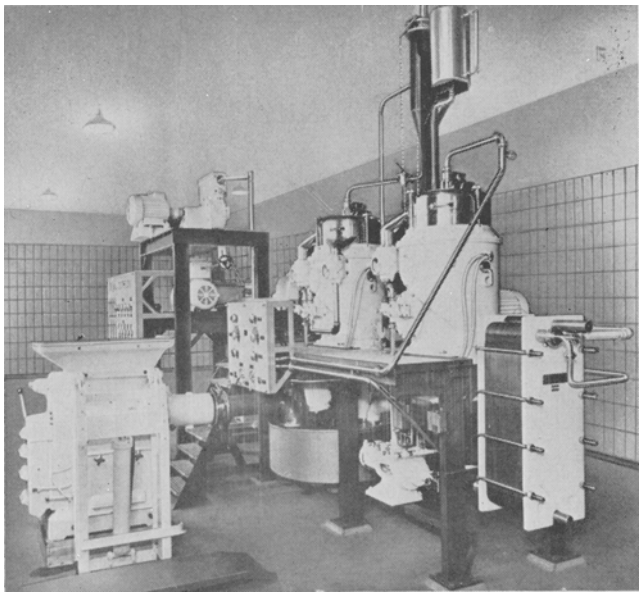

FIG. 4. Typical 8,000 p.p.h. Centriflow rendering plant.

throughout the world, either installed and operating or under construction. Figure 4 shows a typical installation of approximately 8,000 lbs. per hour of raw-fat capacity. This installation is extremely compact and automatized. The hasher in the foreground is equipped with a hydraulic lifter for dumping raw fat into the feed hopper. The raw fat enters the hasher and comes out a purified, cooled fat which discharges from the plate heat-exchanger shown in the right foreground.

Numerous data have been obtained from the many installations when operating on various types of fats producing lard and tallow. This continuous process gives an extremely high yield and a high-quality fat. Table I gives material balance data for an average rendering plant. For an easy means of calculating, a 1,000-lb. basis was used for all data.

The lard fat in this case contained 84.1% fat in the raw material while the tallow stock contained 76.5% fat; the recovery of fat in both cases was 99.5%.

Recent information received from Denmark, where the purified lard from a Centriflow plant was rated by an impartial research institute, gave the following results: peroxide value 0.2 me, free fatty acid 0.08%, and total water 0.16%. Fat content in the cracklings was 4.0%. It was further stated by this same research institute that the Swift Stability Test for average Danish fat was 3.9 hrs. while the Centriflow fat tested 7.0 hrs. There were no antioxidants added in either case.

TABLE I

Test Results from a Centriflow Rendering Plant
(Basis: 1,000 lbs. Raw Material)

	Lard	Tallow
Total fat content of raw material	84.5 %	76.5 %
Weight of final products		
Recovered fat	841.0 lb.	761.0 lb.
Cracklings	73.8 lb.	73.0 lb.
Stickwater[a]	174.2 lb.	253.0 lb.
Total	1089.0 lb.	1087.0 lb.
Cracklings	73.8 lb.	73.0 lb.
Solids	28.7 %	28.4 %
Water	67.2 %	67.8 %
Fat	4.1 %	3.8 %
Fat lost	3.03 lb.	2.77 lb.
Stickwater	174.2 lb.	253.0 lb.
Solids	3.8 %	1.9 %
Water	95.6 %	97.4 %
Fat	0.6 %	0.7 %
Fat lost	1.04 lb.	1.77 lb.
Total loss of fat	4.07 lb.	4.54 lb.
Fat Yield	99.5 %	99.5 %

[a] Contains the condensate from direct steam heating.

Conclusion

It has been shown that the Centriflow Animal Fat Process will continuously render various types of raw fatty tissue and in every case produce a high-quality fat with a high yield. The fat produced shows practically no increase in free fatty acids during processing; the taste is neutral, the color light, the water content extremely low, the insoluble content nil, and the yield generally higher than 99% and quite often over 99.5% of the fat content of the raw material.

Summary

A new process for rendering animal fat employing low temperature and short contact is described. This system gives an extremely high yield of quality fat and at the same time produces cracklings of low fat-content.

The individual pieces of equipment are shown along with their functions, which when combined into the continuous process make for a rendering operation of high efficiency.

Plant operating information and material balances combined with flow sheet and actual plant photographs illustrate the efficiency, ease of operation, and compactness of the Centriflow Animal Fat Process.

REFERENCES

1. Dormitzer, H. C., J. Am. Oil Chemists' Soc., *33*, 471–473 (1956).
2. Vibrans, F. C., J. Am. Oil Chemists' Soc., *26*, 575–580 (1949).

[Received June 23, 1958]

Tocopherol Oxidation in Fats. Hydrogenated Soybean Oil[1]

C. D. EVANS, E. N. FRANKEL, and PATRICIA M. COONEY, Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Peoria, Illinois

STUDIES on the antioxidant behavior of tocopherol have been generally confined to lard primarily because natural tocopherols are essentially absent in this fat. Soybean oil is almost never used for antioxidant evaluations because experience has shown that it does not respond to antioxidant treatments. This lack of response is attributed to the high content of natural tocopherols (0.15%) in soybean oil (14). Few studies have been made on tocopherol loss in autoxidizing soybean oil, hydrogenated soybean oil,

[1] Presented at the 49th annual meeting, American Oil Chemists' Society, Memphis, Tenn., April 21–23, 1958.

or the methyl esters of soybean fatty acids although Golumbic (8) showed that the concentration of tocopherol and the nature and origin of the fat markedly influenced the course of oxidation.

Luckmann and Melnick (10) found a greater tocopherol loss when hydrogenated soybean oil was aerated in iron tubes than in glass tubes. In the previous paper we reported (7) that the initial rate of tocopherol loss in autoxidizing fats is small in highly unsaturated vegetable oils but is appreciable in lard containing added tocopherol. Our studies have indicated that unless peroxide-free oils are used and unless trace metals are adequately complexed before autoxidation is started, widely varying results on tocopherol loss will be obtained. The purpose of the present paper was to study the effect of hydrogenation on tocopherol loss during autoxidation of soybean oil.

Experimental

Commercially refined and deodorized soybean oil was hydrogenated in a Parr [2] pressure-reaction apparatus under mildly selective conditions, using 0.4% nickel catalyst at a temperature of 200°C. and a pressure of 5–10 p.s.i. Hydrogenations were terminated at predetermined levels of hydrogen uptake. A commercially hydrogenated soybean oil of iodine value 76 was also included in the autoxidation study. Polyunsaturated fatty acids were determined in the hydrogenated fats by the 45-min. spectrophotometric method of Brice *et al.* (2).

A control run was made, submitting the original soybean oil to all the conditions of hydrogenation except that nitrogen was introduced into the bomb instead of hydrogen in order to evaluate the trace-metal contamination resulting from the hydrogenation catalyst. The hydrogenated samples were filtered through heavy paper pads with the aid of Filtercel and were clear and free from any trace of turbidity. All samples were re-deodorized at 210°C. for 2 hrs. before the autoxidation tests were started. Citric acid was added on the cooling side of deodorization to the respective samples as a 1% alcoholic solution. Oxidation tests were conducted under A.O.M. conditions. Small samples were removed periodically for analysis by methods described by the authors (6, 7).

During oxidation all of the hydrogenated samples developed a deep-reddish coloration that eventually bleached out near the end of the induction period. Spectral measurements revealed a broad absorption maximum at 460–470 mμ in the oxidized samples that was not present in the initial fats. This red coloration may be attributed to chroman 5–6 quinone, which is formed on the oxidation of fats containing gamma-tocopherol (12).

Results

Initial evaluations showed that the slightly hydrogenated oils were less stable than the original soybean oil. Reduced stability could not be attributed to a loss of tocopherol during hydrogenation, but it was demonstrated that residual nickel catalyst was present in all hydrogenated samples and that it markedly affected the oxidation results. As measured by the peroxide induction point, the stability of the original oil was about 5 hrs., which was extended to 6.5 hrs. by the addition of 0.01% of citric acid. Figure 1

[2] The mention of firm names or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

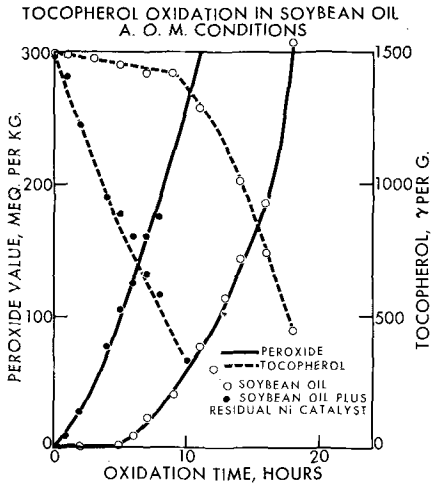

FIG. 1. Tocopherol loss and peroxide development in soybean oil oxidized under A.O.M. conditions.

shows that the catalyst-treated but nonhydrogenated oil was contaminated by residual catalyst, consequently this oil exhibited no induction period. When this same oil was protected by citric acid, a stability equal to that of the original oil was obtained (Figures 1 and 2). Peroxide induction points are the usual indexes employed in measuring stability; however their selection is highly empirical and to a considerable extent dependent upon the judgment of the individual making the selection. An examination of the curves in Figure 3 will illustrate this point.

The loss of tocopherol during autoxidation and its relationship to peroxide development in soybean oil and in oil contaminated with residual catalyst are shown in Figures 1 and 2. The rate of tocopherol destruction in the control oil and in the citric acid-protected oils was slow with a total loss of less than 10% tocopherol over the first 8 to 10 hrs. The induction period was followed by a period at which the rate of destruction of the tocopherol was increased autocatalytically. Time required to reach the break-point in tocopherol destruction is approximately double that required for the peroxide induction period. Usually the tocopherol break-point will be associated with the time at which the peroxide level has accumulated to a value of about 50. The exception is in the

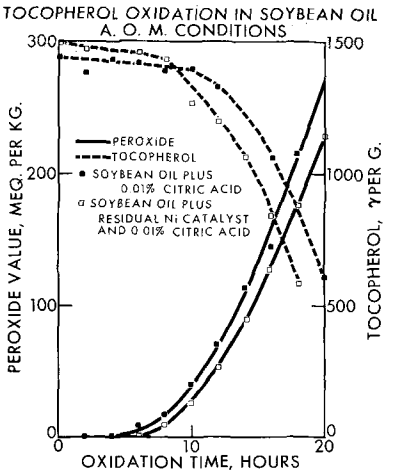

FIG. 2. Effect of citric acid on tocopherol loss and peroxide development in soybean oil oxidized under A.O.M. conditions.

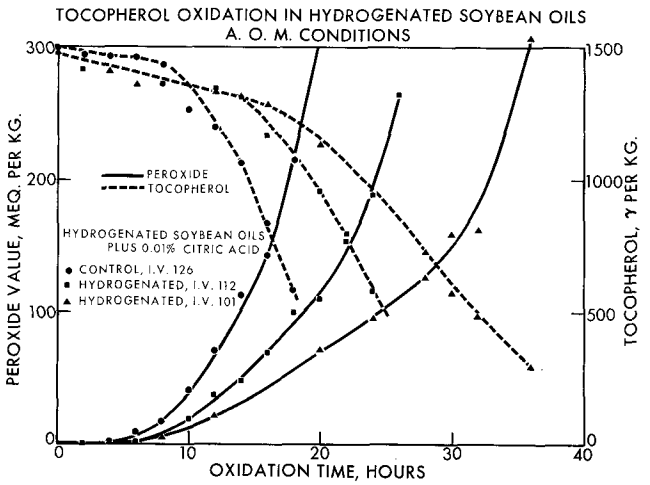

FIG. 3. Tocopherol loss and peroxide development in mildly hydrogenated soybean oil oxidized under A.O.M. conditions.

residual catalyst-contaminated oils where destruction of tocopherol begins immediately and proceeds rapidly until 85 or 90% has been destroyed. In the presence of metal contamination about one-third of the tocopherol was destroyed before a peroxide value of 50 was attained.

Figure 3 shows the loss of tocopherol and the peroxide development in hydrogenated oils which are protected with 0.01% citric acid. Although at iodine values of 112 and 101 the peroxide induction point has not been greatly extended, the peroxides accumulate at a somewhat slower rate. The initial rate of tocopherol loss in these samples was greater than in the nonhydrogenated oil and again did not show a break in the rate of destruction until the peroxide value accumulated to a peroxide level of about 50.

When iodine values of the fat are lowered to 85, 76, and 64, respectively, important differences are immediately apparent in the relationship between the peroxide development and tocopherol destruction curves (Figure 4). At an iodine value of 64, peroxides never accumulate to any extent, and the tocopherol shows a constant rate of loss over the entire period of oxidation. In the commercially hydrogenated sample, with an iodine value of 76, the break

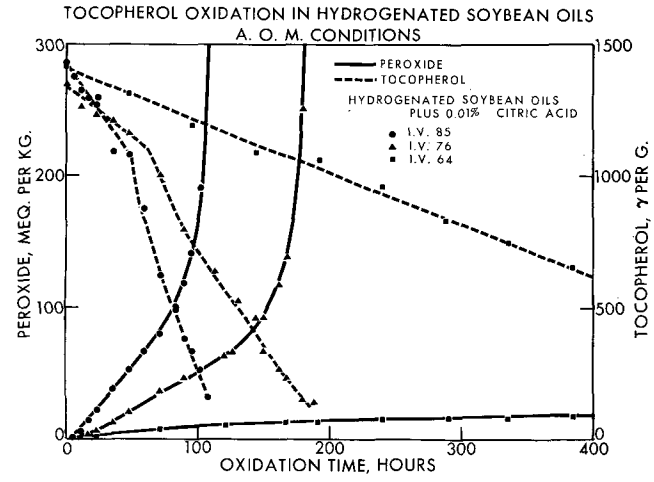

FIG. 4. Tocopherol loss and peroxide development in hydrogenated soybean oil oxidized under A.O.M. conditions.

in the tocopherol curve occurred approximately at a peroxide value of 30. However the initial rate of loss of tocopherol for this sample is in the same order of magnitude and in line with the other hydrogenated samples.

Figure 5 shows the pronounced protection given tocopherol by 0.01% citric acid during autoxidation of a hydrogenated oil (I.V. 85). These results are similar to those obtained in the control oil contaminated with residual catalyst (Figure 1). Similar data (curves not shown) were obtained in all the hydrogenated samples where the loss of tocopherol follows approximately a first-order reaction when metals are present and not inactivated by chelation.

Data obtained from the autoxidation curves are summarized in Table I. Results on vegetable oils (6) showed an increase in the initial rate of tocopherol oxidation with decreased unsaturation of the fats. In

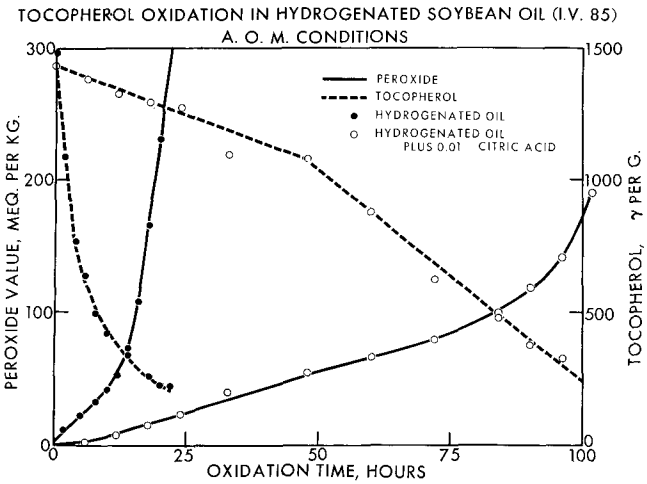

FIG. 5. Effect of citric acid on tocopherol loss and peroxide development in hydrogenated soybean oil.

the present study this relationship was found to exist in hydrogenated soybean oils when the iodine value of the oil was reduced to 101. Below this iodine value the initial rate of tocopherol oxidation decreased as compared with the control soybean oil.

The rapid lowering in the rate of tocopherol loss can be related to the marked decrease in linoleic acid content of the oil. The tocopherol induction point shows an inverse relationship with the linoleic acid content of the sample. Thus the tocopherol induction point disappears with a decrease of linoleic acid although the iodine value is approximately 70. The marked difference in the relative rates of tocopherol oxidation in hydrogenated soybean oil and in lard of similar iodine values can also be accounted for by the elimination of most of the linoleic acid from the hydrogenated fat. In both phases of oxidation it is shown (Table I) that with each decrease in unsaturation the ratio of the rate of tocopherol loss to the peroxide development is increased. This is explained on the assumption of the relatively greater stability of the more saturated fat hydroperoxides and a correspondingly greater chance for reaction with tocopherol. Further basis for substantiating this hypothesis has been obtained by the authors in studies with methyl esters of fatty acids.

TABLE I

Tocopherol Oxidation in Hydrogenated Soybean Oils Autoxidized at 100°C.

Soybean oil samples	Composition			Peroxide development				Tocopherol loss				Ratio of tocopherol loss to peroxide development	
	Iodine value	Linoleic acid	Linolenic acid	Induction period	Peroxide value at end of induction period	Initial rate[a]	Catalyzed rate[b]	Induction period	Peroxide value at end of induction period	Initial rate[a]	Catalyzed rate[b]	Initial	Catalyzed
		%	%	*hrs.*	*me./kg.*	*me./kg./hr.*		*hrs.*	*me./kg.*	*γ/g./hr.*			
Control	126.0	48.6	7.05	5	3.0	1.6	18.0	10	53.8	8.9	89	5.7	4.9
Control + 0.01% citric acid	126.0	48.6	7.05	6	1.9	1.2	18.0	11	54.7	3.6	83	3.1	4.6
Control + residual Ni catalyst + 0.01% citric acid	126.0	49.6	7.80	5	3.8	1.7	17.0	10	41.5	4.0	83	2.4	4.9
Hydrogenated + 0.01% citric acid	112.7	35.4	6.10	6	1.6	0.88	9.1	14	48.4	12.0	71	13	7.8
Hydrogenated + 0.01% citric acid	101.7	23.3	2.28	8	5.9	0.74	6.5	18	56.9	12.1	67	16	10
Hydrogenated + 0.01% citric acid	85.6	7.28	0.12	12	5.7	0.47	1.3	50	53.8	7.4	15	16	12
Hydrogenated[c] + 0.01% citric acid	76.1	4.06	0.05	24	6.4	0.27	0.6	65	30.9	5.3	7.5	20	12
Hydrogenated + 0.01% citric acid	64.1	1.85	0.08	>800	....	0.062	.....	....	.....	2.2	....	36	....

[a] Refers to changes occurring during the induction period.
[b] Refers to changes occurring after the induction period.
[c] Commercial sample of hydrogenated soybean oil.

Discussion

Loss of tocopherol in hydrogenated fat follows an autocatalytic-type curve which shows a distinct induction period (zero-order phase), followed by a period of rapid oxidation. The zero-order phase exists as long as the peroxide value remains approximately below 50. Direct air oxidation of tocopherol in fat systems is negligible (9, 16). Rapid autoxidation of tocopherol occurs only under those conditions where a relatively high level of hydroperoxide has accumulated. The time interval necessary for the buildup of a sufficient free radical concentration, *i.e.*, the hydroperoxide level, is suspected to be related more directly to the linoleic acid content of the system rather than to the iodine value.

Much of the improvement in oxidative stability imparted to soybean oil by hydrogenation may be lost by reason of the amount of residual catalyst remaining in the fat. Loss of oxidative stability in hydrogenated fats with iodine values as low as 80 is shown by both the high peroxide level at the induction point (usually in the P.V. range of 100) and the high loss of tocopherol, approximately 70–80% at the time of the peroxide induction point. Long induction periods are not obtained in soybean oil hydrogenated to commercially usable levels unless the oils are protected by the addition of a metal-inactivating agent. The pronounced effect obtained through chelation in improving stability and in preventing the destruction of tocopherol is well demonstrated in Figures 1 and 5.

Realization of the importance of a trace-metal hydroperoxide catalyst and the function of a metal chelate is fundamental to understanding the mechanism of fat autoxidation. Uri (15) has stated that the free radical reactions are metal-catalyzed and that the kinetics of the reaction indicate molecular complex formation takes place between the metal and oxygen. The evidence of Chalk and Smith (3) indicates that the metal catalyst functions by interaction with the hydroperoxide and not with the substrate. Banks *et al.* (1) have interpreted the final constant rate of oxygen absorption, which is independent of the peroxide content, as being evidence of a unimolecular breakdown of a hydroperoxide metal-catalyst complex. Previously (4) we showed that citric acid is not a sufficiently strong chelating agent to remove iron from the postulated hydroperoxide metal complex, and only at exceedingly high concentrations would citric acid remain effective. With increasing peroxide concentration the formation of the metal hydroperoxide complex is favored over the formation of the citric acid complex. The results of the present study indicate that the catalytic phase of the tocopherol oxidation can be logically explained on the basis of a metal-hydroperoxide complex. Thus the autocatalytic phase of the destruction of tocopherol may be triggered by a sufficient accumulation of stable hydroperoxide, which can cause a rapid release of metal bound by the citric acid chelate. Once the metal is dissociated from the citric acid chelate, the increasing concentration of peroxides would constantly shift the reaction towards the release of more iron.

The rate of tocopherol destruction in a hydrogenated fat that is not protected with a metal inactivator exhibits first-order kinetics. This rate curve is typical of the many published for tocopherol or antioxidant loss in autoxidizing fats (5, 8, 11, 12). Curves of this type are presented as evidence that the loss of antioxidant coincides with the rapid development of peroxides; however the effect of metal contaminants was not considered. Unprotected vegetable oils and lard give this type of curve, and a discussion and interpretation of the results are presented in a separate paper (6). In chelate-protected fats it might be expected that the rates of oxidation of tocopherol, after the induction period, would be the same as in the unprotected sample. This expectation was not found to be true for this series of hydrogenated soybean oils, as can be seen in Figure 5. Apparently the residual effects of the chelate or its complex prevent tocopherol destruction from obtaining the kinetics of a first-order reaction. In nonhydrogenated vegetable oils (Figure 1) the two rate curves appear to be more similar and the chelate-protected oil curve is simply the nonprotected oil curve displaced by the extent of the induction period.

In this series of hydrogenated soybean oil samples the shape of the oxidation curve, after the induction period, changes progressively from a more nearly autocatalytic type of reaction at high unsaturation to a zero-order reaction at low unsaturation. Each curve in the series of oxidations must be looked upon as a composite or summation curve, made up literally of

hundreds of curves representing each type of glyceride molecule present in the substrate. Tocopherol oxidation curves are probably different for each type of glyceride even though iodine values of the substrates are the same. Kinetic studies made on such a heterogeneous substrate as a hydrogenated fat cannot be unequivocally interpreted.

The antioxidant efficiency of natural tocopherol in hydrogenated soybean oil cannot be considered high if it is evaluated in terms of preventing peroxide development. In trace-metal-contaminated fats its effectiveness is low. Uri (15) regards tocopherol as much inferior to butylated hydroxyanisole or propyl gallate, and he does not regard it as the most powerful of the natural antioxidants present in vegetable oils. Peroxides develop to rather high levels for edible fats by the time the rapid autocatalytic stage is reached. In all cases where the fat is protected by citric acid, the peroxide levels are more than 100 before the tocopherol levels are reduced to 50% of their initial value. It must also be borne in mind that the initial tocopherol level in soybean oil is 0.15%, which is higher than that normally used in the evaluation of antioxidants. This level may be pro-oxidant in its effect and higher than the optimum level, which is also a factor in the development of high peroxide levels at the time of the peroxide induction point (11, 13).

Summary

The destruction of tocopherol was studied during autoxidation of a series of hydrogenated soybean oils of decreasing unsaturation. The presence of trace amounts of residual hydrogenation catalyst markedly increased the rates of oxidation of the fat and the destruction of the tocopherol to such an extent that the induction period was entirely eliminated. The catalytic effect of the residual hydrogenation catalyst was eliminated by the use of 0.01% citric acid. Tocopherol autoxidation curves obtained with citric acid-protected fats are typical autocatalytic rate curves showing a distinct induction period. The initial rate of loss of tocopherol is increased at iodine values of 112 and 101, then decreased as the iodine values of the fat are lowered to 90 and below. The time of the tocopherol induction period increases with the decrease in iodine values of the hydrogenated fat.

Increase in the time of the induction period is more closely associated with the linoleic acid content of the fat than to the over-all iodine value. The autocatalytic rates of destruction of tocopherol, *i.e.*, rates beyond the induction period, decreased with the degree of hydrogenation of the fat and show a rapid change at iodine values where a marked lowering of the linoleic acid occurs. When essentially all of the linoleic acid has been removed from the oil, the autocatalytic phase of tocopherol destruction has also been eliminated, and at this iodine value the tocopherol oxidizes at a constant rate.

The disappearance of tocopherol per unit of peroxide accumulated was shown to increase appreciably with the degree of hydrogenation. The greater destruction of tocopherol is attributed to reactions with the more stable fat hydroperoxides, which accumulate to a greater extent in the hydrogenated soybean oil than in the original oil.

Acknowledgment

The technical assistance of C. R. Scholfield in determining the spectral analysis of the fats is gratefully acknowledged.

REFERENCES

1. Banks, G. L., Chalk, A. J., Dawson, J. E., and Smith, J. F., Nature, *174*, 274–275 (1954).
2. Brice, B. A., Swain, M. L., Herb, S. F., Nichols, P. L. Jr., and Riemenschneider, R. W., J. Am. Oil Chemists' Soc., *27*, 279–287 (1952).
3. Chalk, A. J., and Smith, J. F., Trans. Faraday Soc., *53*, 1214–1244 (1957).
4. Cooney, P. M., Evans, C. D., Schwab, A. W., and Cowan, J. C., J. Am. Oil Chemists' Soc., *35*, 152–156 (1958).
5. Filer, L. J. Jr., Mattil, K. F., and Longenecker, H. E., Oil and Soap, *21*, 289–292 (1944).
6. Frankel, E. N., Evans, C. D., and Cooney, Patricia M., manuscript in preparation.
7. Frankel, E. N., Evans, C. D., and Cowan, J. C., J. Am. Oil Chemists' Soc., *34*, 544–546 (1957).
8. Golumbic, Calvin, Oil and Soap *20*, 105–107 (1943).
9. Lips, H. J., J. Am. Oil Chemists' Soc., *34*, 513–515 (1957).
10. Luckmann, F. H., and Melnick, D., J. Am. Oil Chemists' Soc., *32*, 175–176 (1955).
11. Oliver, G. D., Singleton, W. S., and Bailey, A. E., Oil and Soap, *21*, 188–193 (1944).
12. Swift, C. E., Mann, G. E., Fisher, G. S., Oil and Soap, *21*, 317–320 (1944).
13. Swift, C. E., Rose, W. G., and Jamieson, G. S., Oil and Soap, *19*, 176–180 (1942).
14. Thompson, C. R., and Steenback, H., Arch. Biochem. and Biophys., *4*, 15–22 (1944).
15. Uri, N., Chem. and Ind., 515–517 (June 16, 1956).
16. Unpublished data of the authors.

[Received August 7, 1958]

Solubilities of Vegetable Oils in Aqueous Ethanol and Ethanol-Hexane Mixtures[1]

RAMALINGAM KAPARTHI[2] and K. S. CHARI,[3] Department of Chemical Engineering, University of Cincinnati, Cincinnati, Ohio

A RATIONAL APPROACH to the design of an efficient extraction unit to extract vegetable oils from oleaginous materials requires a knowledge of the solubilities of various vegetable oils in the proposed solvent. The published data on the solubilities of oils in ethanol are scanty. Taylor, Larson, and Johnson (10) made a phase-rule study of different systems of oils and alcohols to determine the amount of oleic acid necessary for complete miscibility with 90% alcohol and absolute alcohol at 25°C. Solubilities of soybean oil (4, 9), cottonseed oil (1, 2, 4, 8), peanut oil (4, 8), and other oils, like sesame (4, 8), corn, linseed, and tung oils, are reported in the literature (5, 6). The miscibility data were obtained for different oils by the sealed-tube method (2, 8, 9, 10). The purpose of the present investigation is to determine the solubilities of edible and nonedible indigenous vegetable oils in various concentrations of alcohols at different temperatures It is known that alcohol is a good solvent for oil extraction at elevated temperatures, mostly

[1] Presented at fall meeting, American Oil Chemists' Society, Cincinnati, O., September 30–October 2, 1957.
[2] Present address: Department of Chemical Technology, Osmania, University, Hyderabad, India.
[3] Present address: Regional Research Laboratory, Hyderabad, India.