THE JOURNAL OF THE American Oil Chemists' Society

Volume 33 SEPTEMBER, 1956 No. 9

Stabilization of Edible Animal Fats During Rendering

REX J. SIMS and LEE HILFMAN, Swift and Company, Chicago, Illinois

AN OBVIOUS METHOD of minimizing oxidative deterioration in lard and other edible animal fats is to incorporate phenolic antioxidants at an early stage in the processing. Dugan *et al.* have observed beneficial effects from the stabilization of pork fat with antioxidants during the dry-rendering process (1). Recently a paper has appeared which describes improvements in quality resulting from the stabilization of yellow grease during dry-rendering (2).

The purpose of this study was to determine whether phenolic antioxidants could be used to advantage during the pressure steam-rendering of lard and edible beef fats. Incorporation of the antioxidant directly in the rendering kettle with the tissue has several advantages.

a) The churning and rolling action of the steam provides excellent mixing and assures uniform distribution of the antioxidant throughout the rendered fat.

b) It is not necessary to provide tanks equipped with mechanical agitators and heating coils for the purpose of mixing the fat with antioxidants after rendering.

c) Since the stabilizer is already present when the pressure on the rendering kettle is released, oxidation is minimized during settling and subsequent pumping.

The amount of antioxidant dissolving in the fatty phase during rendering depends upon its being relatively soluble in fat and relatively insoluble in both water and protein. Naturally, best results would be anticipated with the more fat-soluble of the edible antioxidants.

Materials. Lard was rendered from mixed shoulder, ham facing, plate, loin, and back fats. For the laboratory scale tests the fresh cutting fats were diced, mixed thoroughly, wrapped in wax paper, and stored at —20°C. until they could be rendered. None of the tissue was kept for more than three days, and no deterioration was observed during this period at —20°C.

Beef fat was rendered in the laboratory from mixed kidney, ruffle, caul, and cutting tissues. These tissues were ground together, mixed carefully, and stored at —20°C. until they could be rendered.

Antioxidants used in the test work were all of the food-grade type. Percentages given are in all cases based upon the weights of fatty tissue charged to the rendering kettle. The phenolic antioxidants and mixtures used are listed below:

Butylated hydroxyanisole (BHA)

Butylated hydroxytoluene (BHT)

20% propyl gallate and 10% citric acid in 70% propylene glycol (PC)

20% BHA, 6% propyl gallate, and 4% citric acid in 70% propylene glycol (APC)

20% BHA and 20% BHT in 60% cottonseed oil (AT).

Experimental

Laboratory-scale, pressure steam-renderings were conducted in a 2-liter stainless steel, electrically heated, mechanically agitated autoclave. To 1 kg. of diced, mixed fats were added 500 ml. of water and the antioxidants as shown in the various examples given below. In each test the autoclave was vented while the batch was being heated to temperature. When all of the air had been expelled, as evidenced by the appearance of steam, the valve was closed. Heating was continued up to and held at 140°C. and 50 p.s.i. of steam pressure with stirring for a 1-hr. period. The charge was cooled until the pressure inside the autoclave had dropped to atmospheric. Then after the head had been removed, the rendered fat was transferred to a separatory funnel and settled; the water and proteinaceous fines were drawn off. Finally the fat was filtered with suction through diatomaceous earth to remove moisture.

Plant-scale tests were run, using 20,000 pounds of mixed pork cutting fats per batch. The fatty tissues were rendered with antioxidants in carbon steel kettles for 3 hrs. under 50 p.s.i. of steam pressure. When the pressure had been released, the level of the interface was adjusted by pumping in additional water through a valve at the bottom of the tank. Then the lard was gravitated to settling tanks. After several hours of settling representative samples of each batch were filtered through diatomaceous earth and analyzed.

Results

Laboratory Scale Rendering of Lard. The analytical constants obtained on lard samples from two series of laboratory-scale renderings are shown on Tables I and II. Initial peroxide values (3, 4) on all of the freshly rendered lards prepared in these two series were less than 0.1 me./kg. The Lovibond colors of the samples in Table II were all 0.2 red or lighter. These lard samples (180 g. each) were stored at both 98°F. and 140°F. in loosely capped glass jars (4 in. high by 2 in. wide). Peroxide values were determined after 70 days at 98°F. The peroxide values of the

TABLE I

Lard Rendered In Laboratory Autoclave

Antioxidant	AOM Stability[a]	Lovibond Color[b]
	Hours	*Y — R*
None	3	2 — 0.2
0.02% BHA	24	2 — 0.2
0.02% BHT	21	2 — 0.2
0.05% APC	24	2 — 0.2

[a] King, A. E., Roschen, H. L., and Irwin, W. H., Oil & Soap, *10*, 105 (1933); Mehlenbacher, V. C., Oil & Soap, *19*, 137–139 (1942).
[b] A.O.C.S. Official Method Cc 13b-45, Wesson Method using Lovibond glasses.

TABLE II

Lard Rendered In Laboratory Autoclave

Antioxidant	FFA[a] %	AOM Stability	P.V. After 70 Days at 98°F.	Time at 140°F. to Reach PV of 20 me./kg.
		Hrs.	*(me./kg.)*	*Days*
None	0.31	3	30.8	15
0.01% BHA	0.31	28	7.6	32
0.05% PC	0.37	10	3.8	26
0.05% APC	0.35	36	3.4	39
0.05% AT	0.29	38	2.4	81
0.01% BHT	0.33	25	2.8	50
None	0.31	3	32.2	15

[a] A.O.C.S. Official Method Ca 5a-40.

samples stored at 140°F. were determined daily, and the number of days required to reach values of 20 me./kg. are recorded in Table II.

In these laboratory-scale experiments (Tables I and II) satisfactory stabilization was obtained by using either of the antioxidants BHA or BHT at the 0.01% level. With mixtures of BHA and BHT (0.05% AT) the resulting stability was additive in the 140°F. storage test and somewhat less than additive in the AOM test. No synergism was evident between the two phenolics. Propyl gallate (0.01%) with citric acid (0.005%) in propylene glycol (PC) had relatively little stabilizing effect.

Plant Scale Rendering of Lard. In Table III are shown stability data and other analytical constants

TABLE III

Plant Scale Rendering of Lard

Antioxidant	F.F.A.	Initial P.V.	AOM Stability	Lovibond Color
	%	*me./kg.*	*Hours*	*Y — R*
None	0.37	1.7	1	2 — 0.5
0.01% BHA	0.38	0.9	23	2 — 0.9
None	0.33	<0.1	3	3 — 0.5
0.1% BHT	0.33	<0.1	18	3 — 0.5
None	.....	....	4	3 — 0.3
0.043% PC	.....	....	28	5 — 0.3
None	.....	....	3	2 — 0.2
0.043% PC	.....	....	9	3 — 0.3
None	.....	....	2	2 — 0.2
0.043% PC	.....	....	18	3 — 0.3

on batches of lard rendered with antioxidants in plant-scale, pressure steam-rendering equipment. In this series of tests propyl gallate with citric acid in propylene glycol gave somewhat more satisfactory results than were observed in the small scale test reported in Table II. BHA is slightly more effective than BHT at the 0.01% level.

Steam Rendering of Beef Fats. Results obtained in the laboratory-scale renderings of mixed beef fats are given in Table IV. Again propyl gallate with citric acid showed relatively little stabilizing effect. Best results for a given level of antioxidant were observed, using BHA alone. Again no synergism was noted between BHA and BHT or between propyl gallate and BHA.

Stabilization Before vs. After Rendering. It was of practical significance to determine what percentages, if any, of the phenolic antioxidants are lost in the water phase during renderings such as those described above. For this purpose a number of laboratory-scale renderings were conducted in which the A.O.M.s of lards stabilized before and directly after

TABLE IV

Beef Fats Rendered In Laboratory Autoclave

Antioxidant	F.F.A.	AOM Stability	Lovibond Color
	%	*Hours*	*Y — R*
None	0.85	11	35 — 2.0
0.01% BHT	0.90	79	35 — 2.4
0.05% AT	0.80	190	35 — 2.3
0.05% APC	0.70	162	35 — 2.0
0.05% PC	0.80	21	35 — 2.4
0.01% BHA	0.70	170	35 — 2.1

rendering were compared. In each example a portion of the control batch was stabilized immediately after settling and drawing off the aqueous phase. Results of this work are reported in Table V.

It is immediately apparent from the figures shown in Table V that equally satisfactory results were obtained with the individual antioxidants BHA and BHT regardless of the point of addition. With the synergistic mixtures containing BHA and BHT (AT), propyl gallate and citric acid in propylene glycol (PC), or BHA, propyl gallate, and citric acid in propylene glycol (APC), the resulting A.O.M.s are dependent upon when the stabilizer was added. Much better results were found when the lard was stabilized immediately after rendering.

Dry Rendering. A possible explanation for the lack of stabilization shown by an antioxident mixture, such as APC, when added before rendering, is its relatively high solubility in water. To check this possibility a series of dry renderings was carried out, comparing the effectiveness of stabilization before with that after rendering. One-kilogram batches of mixed, ground pork fats were rendered at 70°C. with stirring under 18-mm. pressure. After the tissues had been heated and stirred for 1 hr., the rendered fats were filtered through Filter Cel to remove protein. Results of these tests are shown in Table VI. Even in the absence of large quantities of water, the mixture

TABLE V

Laboratory-Scale Rendering of Lard Stabilization Before vs. After Rendering

Antioxidant	Series 1		Series 2		Series 3	
	AOM (Hours)	IPV (me./kg.)	AOM (Hours)	IPV (me./kg.)	AOM (Hours)	IPV (me./kg.)
Control	1	0.4	5	0.4		
0.01% BHA (after rendering)	10	0.8	21	0.4		
0.01% (before rendering)	11	<0.1	20	0.6		
Control	3	0.4	3	0.6		
0.01% BHT (after rendering)	14	<0.1	16	0.6		
0.01% BHT (before rendering)	14	0.8	15	0.4		
Control	5	0.4	2	<0.1	3	<0.1
0.05% PC (after rendering)	28	0.4	38	0.4	28	<0.1
0.05% PC (before rendering)	14	0.1	4	0.2	10	<0.1
Control	2	<0.1	3	<0.1		
0.05% APC (after rendering)	60	0.6	54	0.6		
0.05% APC (before rendering)	18	0.2	15	0.2		
Control	1	<0.1	3	<0.1		
0.05% AT (after rendering)	43	0.2	40	0.2		
0.05% AT (before rendering)	25	<0.1	20	<0.1		

TABLE VI

Dry Rendering of Lard

Antioxidant	AOM Stability	Initial P.V.	F.F.A.
	Hrs.	*me./kg.*	%
None	5	<0.1	0.25
0.05% APC (after rendering)	37	<0.1	0.26
0.05% APC (before rendering)	30	<0.1	0.24
None	9	<0.1	0.28
0.05% APC (after rendering)	60	<0.1	0.28
0.05% APC (before rendering)	40	<0.1	0.29
None	4	<0.1	0.26
0.05% AT (after rendering)	60	<0.1	0.26
0.05% AT (before rendering)	70	<0.1	0.26
None	2	<0.1	0.35
0.05% AT (after rendering)	36	<0.1	0.31
0.05% AT (before rendering)	35	0.4	0.28

APC still showed somewhat better stabilization, when added after rendering, than it did when added before rendering. With the less water-soluble mixture AT, results before rendering were as good as, or slightly better than, those obtained on adding the stabilizer after rendering.

Effect of Deodorization. It was of interest to determine to what extent the antioxidants added before or shortly after rendering are removed by distillation during steam deodorization. Batches of lard rendered from cutting fats and containing added BHA or BHT were deodorized in all-glass laboratory equipment for 4 hrs. at 220°C. and 1-mm. pressure. BHA was determined in the deodorized oils by the method of Mahon and Chapman (5) and BHT by the method of Austin (6).

Results of this test are recorded in Table VII. Both BHA and BHT are removed almost quantitatively during deodorization.

Discussion of Results

The laboratory- and plant-scale rendering tests described here demonstrate that lard and edible beef fats can be stabilized effectively by incorporating phenolic antioxidants during pressure steam-rendering. The individual phenolics, such as BHA and BHT, provide relatively more protection for a given stabilizer level than do the mixtures containing BHA and BHT in cottonseed oil (AT), propyl gallate and citric acid in proylene glycol (PC), or BHA, propyl gallate, and citric acid in propylene glycol (APC).

TABLE VII

Effect of Deodorization

Antioxidant	Initial P.V.	AOM Stability	Anti-oxidant Found	Lovibond Color
	me./kg.	*Hrs.*	%	*Y* — *R*
None	0.3	1	0.000	7 — 1.2
0.01% BHA (before deodorization)	0.7	1	0.0007	7 — 1.1
0.01% BHT (before deodorization)	0.5	1	0.0001	7 — 1.3
0.01% BHA (after deodorization)	0.4	20	0.01	7 — 1.0
0.01% BHT (after deodorization)	0.5	13	0.01	7 — 1.0

The ineffectiveness of the combinations in propylene glycol such as PC or APC can be explained in part by their relatively high solubility in the aqueous phase. The fact that AT did not produce maximum stability when incorporated before rendering has no obvious explanation. The unusually high stability found when BHA was added to beef fats prior to pressure steam-rendering (Table IV) parallels a similar observation made by Dugan *et al.* (1) with dry rendering.

From the results given in Table VII it is apparent that the stabilizing effects of BHA and BHT are lost completely during steam-deodorization. Obviously then there is little to be gained by adding these antioxidants during or shortly after the rendering step if the fat is to be processed promptly into finished shortening.

However a large proportion of the lard and edible beef fats produced in this country is stored for variable periods and at times under adverse conditions. It is therefore most important to protect these raw materials from the time they are rendered in order to assure the production of shortening of maximum shelf-life.

Summary

Studies have shown that lard and edible beef fats can be stabilized effectively with phenolic antioxidants during pressure steam-rendering. Best results were obtained for a given stabilizer level with the individual phenolics butylated hydroxyanisole and butylated hydroxytoluene. Poorer results were obtained with the mixtures in propylene glycol.

REFERENCES

1. Dugan, L. R. Jr., Marx, L., Ostby, P., and Wilder, O. H. M., J. Am. Oil Chemists' Soc., *31*, 46 (1954).
2. Gearhart, W. M., and Stuckey, B. N., J. Am. Oil Chemists' Soc., *32*, 287–290 (1955).
3. Paschke, R. F., and Wheeler, D. H., Oil and Soap, *21*, 52–57 (1944).
4. Wheeler, D. H., Oil and Soap, *9*, 89–97 (1932).
5. Mahon, J. H., and Chapman, R. A., Anal. Chem., *23*, 8, 1116–1120 (1951).
6. Austin, J. J., "Quantitative Analysis of Butylated Hydroxytoluene (BHT) in Fats and Oils," private communication.

[Received March 26, 1956]

Effect of Free Carboxylic Groups on the Course of Sulfur Trioxide Sulfonation of Unsaturated Fatty Acids[1]

THOMAS W. SAULS and WALTER H. C. RUEGGEBERG, Tennessee Corporation Research Laboratories, College Park, Georgia

IT HAS RECENTLY BEEN SHOWN (1) that the presence of small amounts of simple carboxylic acids, both aliphatic and aromatic, exhibits profound effects on the mechanism of sulfonation of aromatic hydrocarbons with sulfur trioxide in liquid sulfur dioxide. Presumably carboxylic acids destroy intermediate organic pyrosulfonic acids to produce acylsulfonic acids. This results in pronounced reduction in the formation of sulfones which are postulated to form through the reaction between such pyrosulfonic acids and aromatic hydrocarbons. In a more recent disclosure (2) Gilbert and Giolito describe similar results for sulfur trioxide sulfonations of aromatic hydrocarbon conducted in the presence of slightly larger amounts of

[1] Patent covering the reaction products and their preparation has been applied for.