the presence of a wide variety of alkaline salts. Snell and Biffen (9) have described the possible combinations of 12 commercially available alkaline salts. It should be recognized that most of these combinations can be analyzed by this procedure for both carbonate and bicarbonate content.

Summary

Sodium bicarbonate can be determined directly in the presence of sodium carbonate and soap by heating the mixture under controlled conditions. The carbon dioxide liberated by heating is estimated gravimetrically and calculated to sodium bicarbonate. The balance of the carbon dioxide content of the sample is liberated by acid, estimated gravimetrically, and calculated to sodium carbonate. The procedure is applicable in the presence of synthetic detergents. It is rapid and yields accurate results.

REFERENCES

1. Blank and Boggie, Oil and Soap *20*, 125 (1943).
2. Official and Tentative Methods of the American Oil Chemists' Society, 2nd Edition, Official Method Da 19a-42, The American Oil Chemists' Society, Chicago (1946).
3. Kolthoff and Furman, "Volumetric Analysis," Vol. 2, p. 88, John Wiley and Sons, Inc., New York (1929).
4. Hillebrand and Lundell, "Applied Inorganic Analysis," p. 137, John Wiley & Sons, Inc., New York (1929).
5. Waldbauer, McCann, and Tuleen, Ind. Eng. Chem., Anal. Ed. *6*, 336 (1934).
6. Official and Tentative Methods of Analysis of the A.O.A.C., 5th Edition, p. 186, Washington, D. C. (1940).
7. Smith "Analytical Processes," 2nd Edition, p. 238, Edward Arnold & Co., London (1940).
8. Bayliss, "Principles of General Physiology," 4th Edition, p. 196, Longmans, Green and Co., Ltd., London (1927).
9. Snell and Biffen, "Commercial Methods of Analysis," 1st Edition, p. 254, McGraw-Hill Book Co., Inc., New York (1946).

The Use of Antioxidants in Potato Chipping[1]

J. E. MAGOFFIN and R. W. BENTZ[2]

ONE of the most interesting developments in the food field in recent years has been the rapid growth of the potato-chipping industry. Although for some time the cooking of potato chips seemed a logical application for antioxidants, there was no antioxidant available which possessed the ability to "carry through" the frying process. The announcement of butylated hydroxyanisole (2, 3) last year and the demonstration that it possessed remarkable "carry-through" properties in animal fats made available an antioxidant suitable for conducting a study on prolonging the shelf life of potato chips. Accordingly we have undertaken this study in our laboratory and in a local commercial potato-chipping plant.

Preliminary work on the effectiveness of butylated hydroxyanisole and combination antioxidants containing butylated hydroxyanisole were conducted in a laboratory fryer which holds one pound of fat. The temperature of the electrically-heated fryer is controlled by means of rheostats. In each experiment 100 grams of sliced potatoes were fried in one pound of fat. The frying was done in small portions, and the stability studies were made on the last 50 grams fried in each lot. No additions of fat were made in any of these experiments. The large-scale experiments were carried out in a commercial fryer of 600 pounds capacity. This was a batch fryer, and it was necessary to add between 50 and 100 pounds of fat daily, depending upon the amount of potatoes fried. In the large-scale experiments up to 5,000 pounds of potatoes were fried before the fryer was emptied and the fat discarded.

Since this study was concerned with the shelf life of potato chips, the bulk of our data consists of results from Schaal Oven (1) studies on the chips themselves.[3] We also investigated the stability of the frying fats by means of the Active Oxygen Method (5) in an attempt to find out how their stability changed with usage. The data obtained in one series of commercial runs are shown in Figure 1. An examination of Figure 1 reveals an apparent decrease in the quality of the fat, as shown by the Schaal tests on the potato chips, and an apparent increase in the quality of the fat, as shown by the Active Oxygen Method tests on the frying fat itself. This contradictory data indicates again the fact that the value of the Active Oxygen Method (A.O.M.) is dependent largely upon the previous history of the fat. Although the A.O.M. is usually applicable to the evaluations of "fresh" fats, this method is not truly indicative of the conditions of fats which have been subjected to high temperature frying over long periods of time.

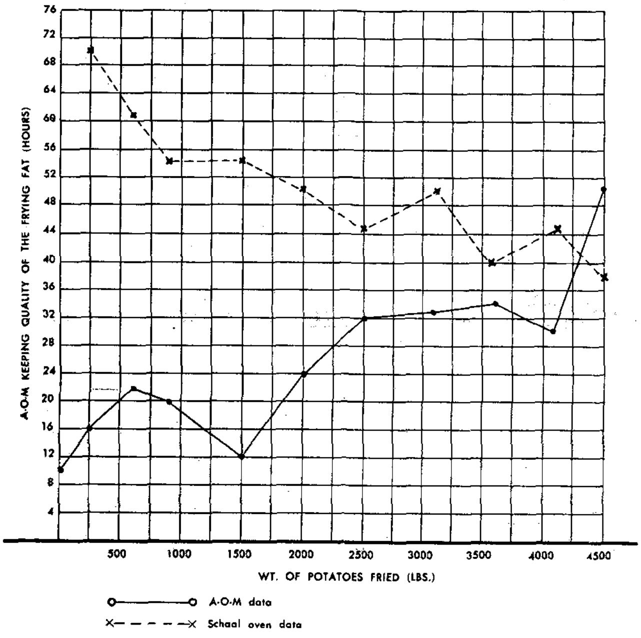

FIG. 1. Relatons of A.O.M. values of frying fats to chip stability. Fat mixture of 60% vegetable shortening—40% lard containing 0.020% butylated hydroxy anisole. Active oxygen method to a peroxide value of 20.

We also made attempts to determine the consump-

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[1] Presented at 23rd Fall Meeting, American Oil Chemists' Society, Chicago, Ill., Oct. 31, Nov. 1 and 2, 1949.

[2] Tennessee Eastman Corporation, Kingsport, Tenn.

[3] The Schaal Oven Tests were conducted at 145°F.

tion of antioxidants during the course of frying experiments. The analytical method used was a modified form of the one described by W. O. Lundberg and H. O. Halvorson (4). Approximately 7.5 grams of fat were dissolved in 25 milliliters of petroleum ether, and this solution was given 5 consecutive washings with 15 milliliter portions of 80% ethanol. The few tiny fat globules which transferred to the ethanol layer were removed by filtration. This modified extraction procedure enabled more complete recovery of the total antioxidant content of the fat.

IT appears that the antioxidant is consumed or removed from the oil by three processes: The first by steam distillation; the second by absorption in the chip; and the third by the normal process of consumption in performing its antioxidant role. With regard to the removal of antioxidant by the potato chip, the analytical results indicate the fat removed with the potato chip contains a somewhat lower percentage of antioxidant than the fat remaining in the fryer.

TABLE I

Apparent Changes in Antioxidant Concentration During Frying

Total Antioxidant Content (Per Cent of Fat) and Schaal Oven Life[1]

Weight of Potatoes Fried (Pounds)	Control Vegetable Shortening		
	Frying Fat, %	Chip Fat,[3] %	Schaal Life of Chips (Days)
0	.008	....	....
500	.006	.005	56
1,000	.004	.004	49
1,500	.003	.003	45
2,000	.002	.003	44
2,500	.002	.003	34
3,000	.002	.003	37
3,500	.002	.003	41
4,000	.001	.002	38
4,500	.002	.002	36
5,000	.001	.002	32

Weight of Potatoes Fried (Pounds)	Stabilized Vegetable Shortening[2]		
	Frying Fat, %	Chip Fat,[3] %	Schaal Life of Chips (Days)
0	.026	....	....
500	.014	.010	75
1,000	.008	.006	70
1,500	.008	.007	61
2,000	.005	.005	65
2,500	.004	.002	56
3,000	.004	.001	59
3,500	.006	.001	63
4,000	.002	.001	62
4,500	.004	.004	53
5,000	.004	.003	57

[1] Per cent total antioxidant in the fat equals natural plus added antioxidants.

[2] Vegetable shortening containing 0.020% butylated hydroxy anisole.

[3] Fat extracted from the chips.

As is evident from the data shown in Table I, an analysis of the apparent antioxidant concentration of a fat being used for deep-fat frying is not a sufficient indication in itself of the stability of that fat or of the stability of products fried in that fat. While apparent antioxidant concentration is useful information, it must not be relied upon as an exclusive characterization.

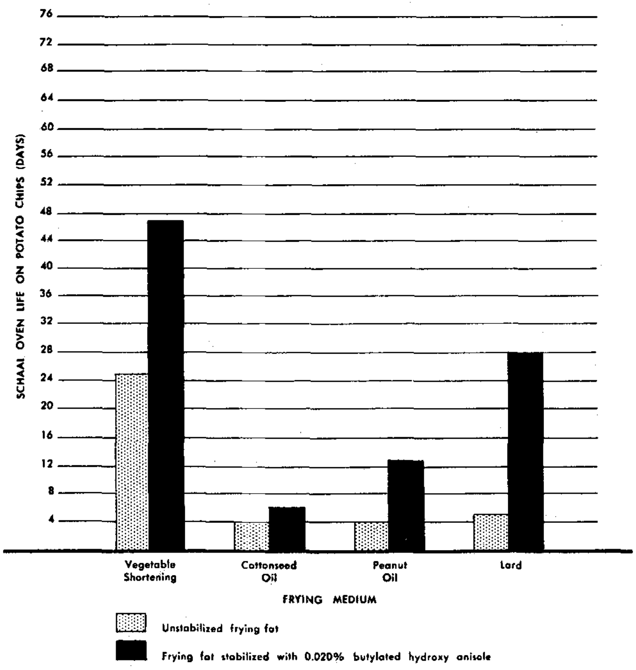

FIG. 2. Laboratory experiments on butylated hydroxy anisole in "single" fats.

In the laboratory potato chips have been fried in hydrogenated cottonseed oil (which hereafter will be referred to as vegetable shortening), refined cottonseed oil, peanut oil, and lard. Fryings also have been made in combinations of vegetable shortening and lard, vegetable shortening and cottonseed oil, and vegetable shortening and peanut oil. Figures 2, 3, 4, and 5 present Schaal Oven data on chips fried in our laboratory experiments. In the absence of antioxidants it is to be observed that vegetable shortening provides the longest stability while a mixture of vegetable shortening and lard comes next in line. These are followed then by mixtures of vegetable shortening and vegetable oils and finally by the individual vegetable oils and lard.

When 0.020% butylated hydroxyanisole is added to the fat before frying, the vegetable shortening-lard blend achieves a stability equal to that of vegetable

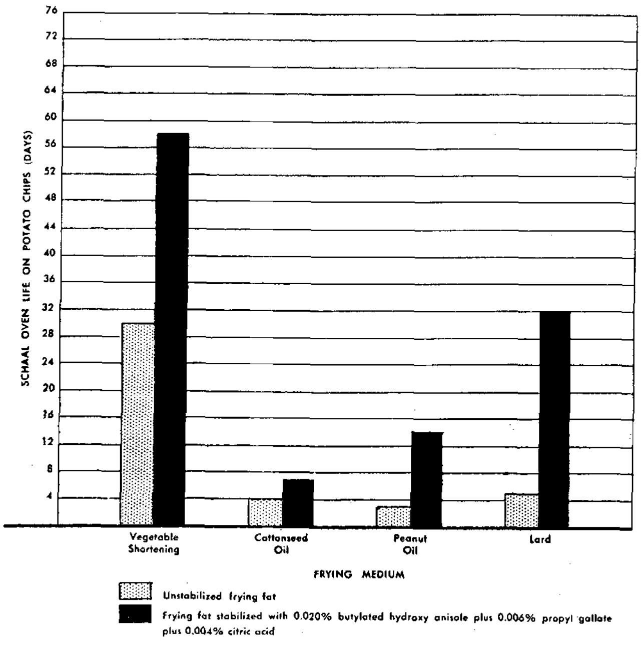

FIG. 3. Laboratory experiments on butylated hydroxy anisole—propyl gallate—citric acid in "single" fats.

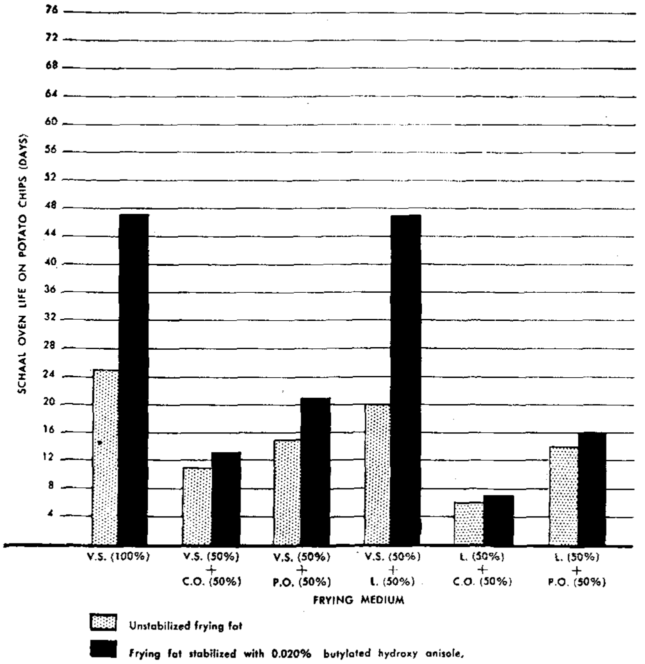

Fig. 4. Laboratory experiments on butylated hydroxy anisole in "mixed" fats. V.S. = vegetable shortening; C.O. = cottonseed oil; P.O. = peanut oil; L = lard.

shortening itself. This is followed by pure lard, and then by the combinations and individual vegetable oils. It is interesting to note that while pure lard is benefited the most by the addition of butylated hydroxyanisole, quite considerable increases in stability have been conferred upon vegetable shortening, the vegetable oils, and the mixtures of vegetable oils with vegetable shortening. The "carry-through" properties of butylated hydroxyanisole seem to be least effective in cottonseed oil and in mixtures containing cottonseed oil.

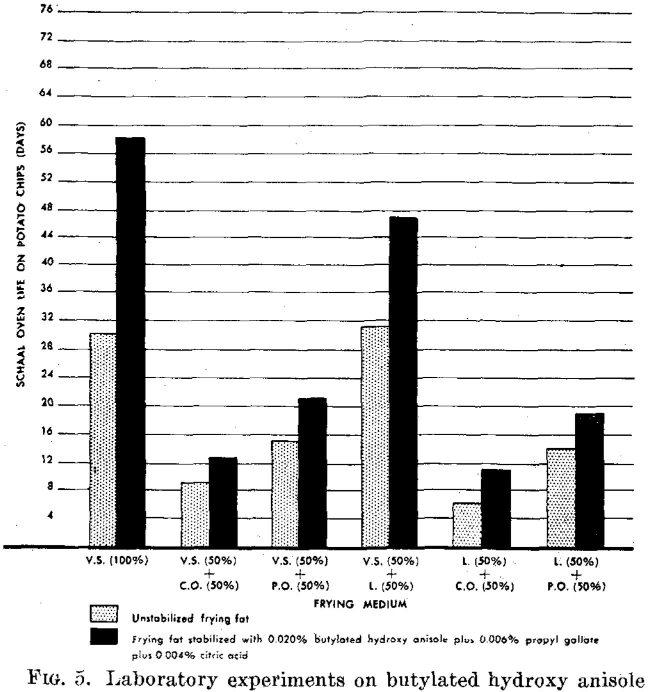

Fig. 5. Laboratory experiments on butylated hydroxy anisole—propyl gallate—citric acid in "mixed" fats. V.S. = vegetable shortening; C.O. = cottonseed oil; L = lard; P.O. = Peanut oil.

A combination antioxidant, consisting of butylated hydroxyanisole, propyl gallate, and citric acid, dissolved in propylene glycol, produced results quite similar to those obtained with butylated hydroxyanisole alone. The final concentrations of antioxidant materials here are 0.020% butylated hydroxyanisole, 0.006% propyl gallate, and 0.004% citric acid. Figures 3 and 5 present Schaal Oven data on this synergistic combination. These relatively small amounts of propyl gallate and citric acid resulted in an additional increase of shelf life in the final product. Experiments in which larger amounts of propyl gallate were used indicate that no additional gain in shelf life of potato chips results when the propyl gallate is increased beyond 0.006%.

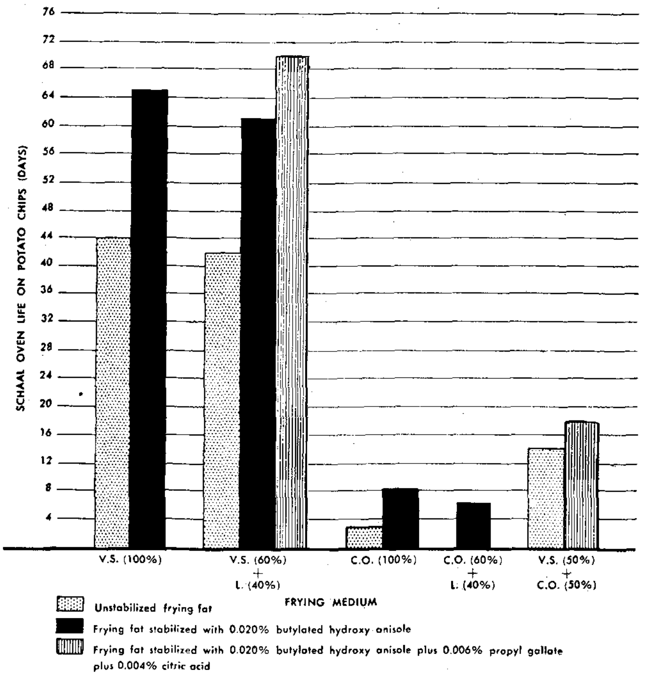

Fig. 6. Commercial experiments on butylated hydroxy anisole and butylated hydroxy anisole—propyl gallate—citric acid. V.S. = vegetable shortening; C.O. = cottonseed oil; L = lard.

The consistent effectiveness of butylated hydroxyanisole demonstrated in laboratory runs made it desirable to conduct some experiments on a larger scale. Accordingly, arrangements were made with a local producer of potato chips to conduct evaluations of antioxidants under commercial chipping conditions. Since it was desired to sell these chips to the general public, only those fat combinations which gave promise in the laboratory of providing chips of suitable stability and taste were used. The fryer used for this experimental work already has been described, as also has been the amount of fat used and the manner in which fat additions were made. Each experiment was carried out over a period of at least seven days of actual operation. In all cases the Schaal Oven life data were obtained on a composite sample of chips from each day's production. The stability value given for each fat is an average of data for 3,000 pounds of potatoes.

The data obtained in the commercial runs is given in Figure 6. These data show that butylated hydroxyanisole, alone or in combination with propyl gallate and citric acid, is an effective antioxidant for cooking potato chips in vegetable oils, vegetable shortening, and combinations of these with lard. Particular attention should be called to the combination of 60% vegetable shortening and 40% lard. This produced a chip of stability approximately equal to that cooked in vegetable shortening and of far superior stability to chips fried in cottonseed oil alone or in a vegetable shortening-cottonseed oil blend. The ratio of 60% vegetable shortening to 40% lard was decided upon after several laboratory experiments with varying percentages of lard in the frying fat. Forty per cent lard seems to be an optimum for best processing characteristics and flavor of final product. Of equal interest is the fact that the life of potato chips fried in pure cottonseed oil can be doubled by the use of butylated hydroxyanisole as antioxidant. It also should be pointed out that, in the one set of experiments where direct comparison is possible, the use of the combination antioxidant provided slightly greater stability in potato chips than the use of butylated hydroxyanisole alone.

Summary

Laboratory and commercial-scale fryings of potato chips have been made with various vegetable oils, vegetable shortenings, lard, and combinations of these. Fryings have been made with and without the addition of butylated hydroxyanisole as an antioxidant. The data from both types of experiments indicates that butylated hydroxyanisole possesses "carry-through" antioxidant properties not only in animal fats but in vegetable oils and vegetable shortenings also. Data also indicates that the addition of propyl gallate and citric acid as synergists to the butylated hydroxyanisole increases the "carry-through" antioxidant properties.

REFERENCES

1. Joyner, N. T., and McIntyre, J. E., Oil and Soap, *15*, 184-186 (1938).
2. Kraybill, H. R., Beadle, B. W., Vibrans, F. C., Swartz, V., Wilder, O. H. M., and Rezabek, H., American Meat Institute Foundation, University of Chicago, Bulletin No. 2, April 1948.
3. Kraybill, H. R., Dugan, L. R., Jr., Vibrans, F. C., Swartz, V., and Bondi, V., American Meat Institute Foundation, University of Chicago, Bulletin No. 4, January 1949.
4. Lundberg, W. O., and Halvorson, H. O., Proc. Inst. Food Tech., 115-126 (1945).
5. Riemenschneider, R. W., Turer, J., and Speck, R. M., Oil and Soap, *20*, 169-171 (1943).

The Synthesis of 12-Ketostearic Acid

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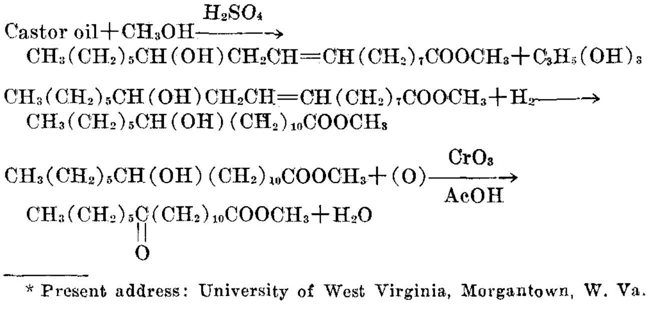
A MAJOR trend in fat and oil technology is the commercial development of valuable chemical derivatives. In addition to acids of increasing degrees of purity, such acid derivatives as amines, amides, and nitriles are now available. A variety of non-ionic surface active agents are being made directly or indirectly from fatty acids. Castor oil is a well known raw material for the synthesis of n-heptaldehyde, octanol-2, and sebacic acid.

Our need for a saturated long-chain keto acid with the ketone group close to the center of the chain stimulated a study of the possibility of making 12-ketostearic acid from castor oil. While such a synthesis is not new (1), the literature showed that detailed directions for a laboratory scale preparation were not available. Since this acid may be of interest to others and since this preparation may point the way to larger scale production, the method is given here.

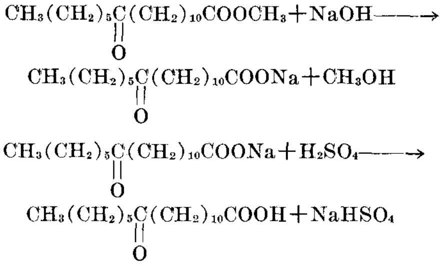
This preparation involves the methanolysis of castor oil to methyl ricinoleate, catalytic reduction to methyl-12-hydroxystearate, oxidation by chromic acid to methyl-12-ketostearate, and saponification and acidification to give 12-ketostearic acid:



$$\text{Castor oil} + CH_3OH \xrightarrow{H_2SO_4} CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7COOCH_3 + C_3H_5(OH)_3$$

$$CH_3(CH_2)_5CH(OH)CH_2CH{=}CH(CH_2)_7COOCH_3 + H_2 \longrightarrow CH_3(CH_2)_5CH(OH)(CH_2)_{10}COOCH_3$$

$$CH_3(CH_2)_5CH(OH)(CH_2)_{10}COOCH_3 + (O) \xrightarrow[AcOH]{CrO_3} CH_3(CH_2)_5\underset{\underset{O}{\|}}{C}(CH_2)_{10}COOCH_3 + H_2O$$



$$CH_3(CH_2)_5\underset{\underset{O}{\|}}{C}(CH_2)_{10}COOCH_3 + NaOH \longrightarrow CH_3(CH_2)_5\underset{\underset{O}{\|}}{C}(CH_2)_{10}COONa + CH_3OH$$

$$CH_3(CH_2)_5\underset{\underset{O}{\|}}{C}(CH_2)_{10}COONa + H_2SO_4 \longrightarrow CH_3(CH_2)_5\underset{\underset{O}{\|}}{C}(CH_2)_{10}COOH + NaHSO_4$$

Experimental

Dissolve 4 g. of concentrated sulfuric acid in 300 ml. (237 g., 7.4 moles) of methanol (99-100% pure). To this solution add 200 g. (0.21 mole) of a refined grade of castor oil. (The average molecular weight of castor oil was considered to be 940.) This mixture is refluxed on the steam bath for four hours with occasional shaking, cooled, and poured into one liter of water with stirring. The oil layer is washed with 100-ml. portions of water until the wash water is neutral to litmus. This washing step is important because residual traces of sulfuric acid will catalyze dehydration of the methyl ricinoleate during distillation.†

The crude methyl ricinoleate is distilled at 3- to 4-mm. pressure, discarding the first 25 ml. and collecting as product the 170-195° fraction. The distillate weighs 150-160 g., which is an 87-93% yield based on the assumption of an 87% concentration of ricinoleic acid in the castor oil (1a).

Analysis of the methyl ricinoleate by saponification number (A.O.C.S. Official Method Cd 3-25),

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† One authority has pointed out that an alkali-catalyzed methanolysis would have the advantage of simplifying this washing step and reducing the danger of dehydration.