method will supply and not to compare the rate of extraction of oil from the four different materials. These extraction rates can be compared only in a general way because the residual oil in the different materials was not determined by the same procedure. In addition, while the residual oil percentages for both meats and seed are expressed on a pure meats basis, the percentages for the prepressed materials are based on solids containing hull particles.

Although the use of the extractor on rolled whole cottonseed has been mentioned only briefly for the reasons stated earlier, the extractor was a valuable tool in exploring the effects of heating before rolling, moisture, and flake thickness upon the extractability of the oil from this material. Use of the basket extractor greatly reduced the number of runs which had to be made with the pilot plant extractor.

Commercial hexane was the only solvent used in any experiments; however other appropriate solvents could be used.

Summary

The equipment and the method have been described for measuring the rate of extraction of oil from oil-bearing materials by solvent. The method consists essentially of immersing wire baskets containing the oil-bearing material in a circulating stream of solvent for varying periods of time. After extraction, the baskets are centrifuged to remove excess solvent, and the residual oil in the solids is determined. The method is patterned after one devised by Boucher *et al.* (1) but has been modified and extended to other oil-bearing materials.

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The Glycerolysis of Fat in Tertiary Aromatic Nitrogeneous Bases to Increase Monoglyceride Yield

KARL F. MATTIL and REX J. SIMS, Swift and Company, Chicago, Illinois

THE interesterification of fats with glycerol at elevated temperature yields a mixture of mono-, di-, and triglycerides and unreacted glycerol. In commercial practice the yield of the desirable, surface-active monoesters (1) is always less than 50% because of the limited mutual solubility of the reactants (2).

In the past a number of solvents have been proposed to increase this solubility (3), and claims for increased yields have been cited in a number of patents (4, 5). In general, these have not proved satisfactory. For example, phenol (3, 4) acts not only as a solvent but enters into the reaction to an undetermined extent. Others have proposed dioxane (5), but in our laboratory we have not been able to duplicate the reported yields.

Consequently a survey of various solvent types was undertaken, and it was found that pyridine, in the presence of catalytic amounts of sodium methoxide, will slowly dissolve fat and glycerol simultaneously even at room temperature. If the mixture is warmed to steam bath temperature, solution takes place in a few minutes.

Yields of monoglycerides above 70%, as measured by the periodic acid titration of Pohle and Mehlenbacher (6), are obtained in these homogeneous mixtures. The maximum yield obtained in this series of experiments, run under a variety of conditions, was 79%. Although this does not compare very favorably with the 90-95% available through molecular distillation (7), this method has certain advantages of simplicity.

Specifically the method involves mixing fats with at least 0.5 part of glycerol by weight, 4 parts by weight of solvent, and at least 0.003 part of catalyst. In the temperature range of 80-100°C. homogeneity and a maximum percentage of monoesters are attained in about 5 minutes, and the product can be isolated immediately thereafter by neutralizing the catalyst with mineral acid, distilling the solvent at reduced pressure, and settling the excess glycerol. Without a solvent the reaction requires several hours at much higher temperature for completion, and then only 40-50% of monoesters results.

The proportions used in the solvent process are critical. If the glycerol-fat weight ratio is cut below 0.5, yields over 60% are not obtained. The solvent-fat ratio must be at least 4:1, or else an extended heating period is necessary. Below 2:1 it is difficult to obtain homogeneity, and the yields are low even after several hours of refluxing.

Solvents other than pyridine which have been tested and found to be satisfactory include γ-picoline, β-picoline, 2,6-lutidine, quinoline, and isoquinoline. With α-picoline, for some obscure reason, the yields are low.

The products can be given a short deodorization at 200°C. without deterioration. In fact, the percentage of monoesters usually increases slightly due to the removal of free glycerol.

Experimental

Table I summarizes data on a series of monoglyceride preparations using various fats in several different heterocyclic nitrogeneous aromatic solvents. The experiments are reported in more detail in the following section.

High gravity glycerol was used in all the preparations. The pyridine was denaturing grade while the α-, β-, and γ-picolines, 2,6-lutidine, and isoquinoline were practical grade reagents obtained from Eastman Kodak Company. The quinoline, also a practical grade material, was distilled under reduced pressure prior to its use.

1. One part of oleo oil and one part of glycerol were mixed with 2 parts of pyridine, to which was added

TABLE I

Experiment No.	Fat	Solvent	Weight Ratios						Yield, % monoglycerides
			Fat	Glycerol	Solvent	Sodium methoxide	Time	Temp. °C.	
1	Oleo oil	Pyridine	1	1	2	0.006	4 hours	100	76.3
2	Lard flakes	Pyridine	1	2.2	6	0.01	16 hours	70	76.9
3	Soybean hard fat	Pyridine	1	1	5	0.02	5 min.	80	77.0
4	Soybean hard fat	Pyridine	1	1	2	0.003	5 min.	80	77.5
5	Soybean hard fat	Pyridine	1	0.5	2	0.02	5 min.	80	65.1
6	Soybean hard fat	Pyridine	1	1	4	0.01	5 min.	90	76.4
7	Soybean hard fat	Pyridine	1	1	3	0.01	1 hour	120	78.0
8	Bleached soybean oil	Pyridine	1	1	4	0.02	4 days	30	73.2
9	Soybean hard fat	γ-Picoline	1	1	4	0.04	5 min.	85	63.6
10	Soybean hard fat	Quinoline	1	1	5	0.04	5 min.	120	68.4
11	Bleached cottonseed oil	Isoquinoline	1	2	6	0.02	1 hour	100	60.7
12	Bleached cottonseed oil	2,6-Lutidine	1	2	6	0.02	1 hour	100	53.0
13	Bleached cottonseed oil	β-Picoline	1	2	6	0.02	1 hour	100	63.7
14	Bleached cottonseed oil	α-Picoline	1	2	6	0.02	1 hour	100	11.0
15	Oleo oil	Dioxane	1	1	2	0.01	4 hours	Reflux	16.5
16	Soybean hard fat	Pyridine	1	1	1	0.01	1 hour	130	28.3
17	Soybean hard fat	Pyridine	1	4	6	0.01	3 hours	100	32.6

0.6% sodium methoxide (based on weight of oil). This mixture became homogeneous after one-half hour of heating on the steam bath. After 4 hours at steam bath temperature and overnight at room temperature the catalyst was neutralized with dilute acetic acid, and the pyridine was removed by washing with salt water. The reaction product contained 76.3% monoglycerides by analysis (6).

2. One part of 60 titer hydrogenated lard, 2.2 parts of glycerol, 6 parts of pyridine, and 0.01 part of sodium methoxide were held at 70°C. overnight. The mixture appeared homogeneous in the first half hour, but the longer time was used to assure equilibrium. This product contained 76.9% monoglycerides.

3. A mixture of 100 g. of soybean hard fat, 100 g. of glycerol, 500 g. of pyridine, and 2 g. of sodium methoxide was held at 80°C. for 5 minutes. The resulting solution was washed with excess dilute hydrochloric acid and then with hot salt water. The product which separated, after being dried at 100°C. and 30 mm., contained 77.0% monoglycerides.

4. A mixture of 50 g. of soybean hard fat, 200 g. of glycerol, 400 g. of pyridine, and 0.15 g. of sodium methoxide was treated as in Example 3. Analysis showed 77.5% monoglycerides in the product.

5. Another mixture containing 100 g. of soybean hard fat, 50 g. of glycerol, 200 g. of pyridine, and 2 g. of sodium methoxide was treated as in Example 3. Found 60.0% monoglycerides in the product. This material was deodorized at 200°C. and 1 mm., holding it at this temperature for 15 minutes and then cooling rapidly. Analysis then showed 65.1% monoglycerides.

6. After heating a mixture of 100 g. of soybean hard fat, 100 g. of glycerol, 400 g. of pyridine, and 1 g. of sodium methoxide for 5 minutes at 90°C., it became homogeneous. Then the catalyst was neutralized with concentrated hydrochloric acid, the pyridine was distilled off at 30 mm., and the glycerol layer was separated. After washing the product with salt water, it was dried *in vacuo*. Found 76.4% monoglycerides.

7. A mixture of 100 g. of soybean hard fat, 100 g. of glycerol, 300 g. of pyridine, and 1 g. of sodium methoxide was held at 120°C. for 1 hour. The product, which was isolated as in Example 6, contained 78% monoglycerides.

8. A mixture of 50 g. of refined and bleached soybean oil, 50 g. of glycerol, 200 g. of pyridine, and 1 g. of sodium methoxide was allowed to stand at room temperature for 4 days. Isolation as in Example 3 yielded a product containing 73.2% monoglycerides.

9. From 100 g. of soybean hard fat, 100 g. of glycerol, 400 g. of γ-picoline, and 4 g. of sodium methoxide, held at 85°C. for 5 minutes, was obtained a concentrate containing 63.6% monoglycerides (isolation as in Example 3).

10. When quinoline was substituted for γ-picoline in Example 9, 500 g. was used at 120°C. The concentrate contained 68.4% monoglycerides.

11. From 100 g. of bleached cottonseed oil, 200 g. of glycerol, 600 g. of isoquinoline, and 2 g. of sodium methoxide, heated to 100°C. for 1 hour, was obtained a product containing 60.7% monoglycerides. After the catalyst had been neutralized and the concentrate had been washed with salt water, the excess solvent was distilled at 1 mm. prior to analysis.

12. Substitution of an equal amount of 2,6-lutidine for the isoquinoline of Example 11 yielded a product containing 53.0% monoglycerides.

13. When an equal amount of β-picoline was substituted for the isoquinoline of Example 11, a concentrate was produced containing 63.7% monoglycerides.

14. With α-picoline substituted for isoquinoline as in Example 11, the percentage of monoglycerides in the product was only 11.0%.

15. A mixture of 50 g. of oleo oil, 50 g. of glycerol, 100 ml. of dioxane, and 0.5 g. of sodium methoxide would not become homogeneous at the boiling point of the mixture even after several hours. Isolation in the usual manner gave a product containing 16.5% monoglycerides.

16. A mixture of 100 g. of soybean hard fat, 100 g. of glycerol, 100 g. of pyridine, and 1 g. of sodium methoxide was held at 130°C. for one hour, but it did not become homogeneous. Isolation as in Example 3 yielded a product containing only 28.3% monoglycerides, presumably due to an inadequate quantity of solvent in the original reaction mixture.

17. A mixture of 100 g. of soybean hard fat, 400 g. of glycerol, 600 g. of pyridine, and 1 g. of sodium methoxide was held at 100°C. for 3 hours. Then it was cooled to room temperature without neutralizing the catalyst. The precipitate was suction-filtered and dried at 100°C. and 30 mm. Found 32.6% monoglycerides. From this it is evident that the catalyst must be destroyed while the solution is still homogeneous if maximum yields are to be obtained.

Summary

A method has been described for producing monoglyceride concentrates containing up to 78% of monoesters. It involves the interaction of fat with glycerol in a tertiary aromatic nitrogeneous base such as pyridine, β- or γ-picoline, 2,6-lutidine, quinoline, or iso-

quinoline, and employs an alkaline interesterification catalyst such as sodium methoxide.

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The Flavor Problem of Soybean Oil. X. Effects of Processing on Metallic Content of Soybean Oil

C. D. EVANS, PATRICIA M. COONEY, HELEN A. MOSER, J. E. HAWLEY, and E. H. MELVIN,
Northern Regional Research Laboratory,[1] Peoria, Illinois

IN a previous publication (1) data were presented, showing the serious effect which trace metal contamination has upon the stability of soybean oil. Spectrographic analysis showed that practically all soybean oils contained iron and copper in amounts which could be definitely detrimental to the stability of the oil. Since this work was reported we have extended our studies and have also included the examination of a number of crude oils. The spectrographic method (2) described previously was employed for the iron and copper analysis, and the organoleptic evaluations were made by our regular published procedure (3).

Through the cooperation of several soybean oil processors we have been able to examine a great number of oil samples taken from each of the unit processes employed in the extraction and refining of soybean oil.

Figure 1 summarizes the data obtained for commercial oils and shows the concentrations of iron and copper that were found in refined, deodorized, and crude edible oils. The oils examined included, besides soybean oil, cottonseed, corn, safflower, sunflower, and sorghum oils. As judged from the limited number of samples examined, there appears to be no difference in the metal contents of these different types of oils. This conclusion is further substantiated by the data presented by O'Connor *et al.* (4) for the crude oils of cottonseed, peanut, rice, okra, and calabash seeds.

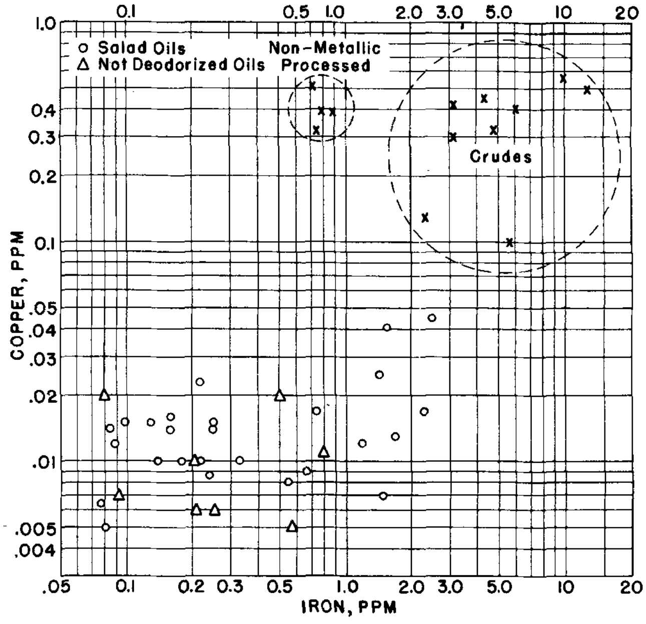

FIG. 1. Iron and copper content of commercially processed edible oils.

TABLE I

Metal Contents and Stability Evaluations of Soybean Oil Sampled From Units of Two Commercial Extractors

Sample Description	Metal Content p.p.m.				Stability		
	Iron		Copper		A.O.M.[a] 8 Hours	Flavor Score	
	Crude	Refined	Crude	Refined	100°C.	0	4 Days
Company A							
Miscella	2.70	.088	.16	.002	5.5	8.9	7.2
Falling film	3.80	.12	.26	.012	1.8	8.5	7.7
Stripper	5.60	.13	.10	.008	1.9	7.8	6.9
Control 176E	......	.015	......	.006	19.4	8.3	6.1
Company B							
Miscella	3.55	.077	.21	.011	17.8	8.9	7.0
Horizontal	4.10	.10	.50	.006	11.4	8.9	6.9
Falling film	4.70	.11	.33	.012	16.0	8.5	7.0
Stripper	2.10	.11	.28	.009	14.7	8.7	6.9

[a] Peroxide value milliequivalents of peroxide per kg. of fat.

The average iron content for laboratory-refined soybean oil has been reported at 0.12 p.p.m.; for commercial undeodorized oils, 0.19 p.p.m.; and for deodorized oils, 0.91 p.p.m. (1). The iron content of crude soybean oils will vary from 2 to 10 p.p.m. while samples of badly contaminated crudes will run from 10 to 100 p.p.m. or more.

The copper content has shown less than a 10-fold variation, and most crude oils will have between 0.2 and 0.5 p.p.m., and the refined oils less than 0.02 p.p.m. Because of the high copper content found when beans are processed in all-glass equipment, it is believed that most of the copper is "native" to the oil. The native copper is more than likely tightly complexed, or at least bound in such a manner that it is not free to act as an oxidation catalyst. "Native" iron and possibly some of the contaminating iron may be complexed with the phosphatides in the crude oil. Our analyses however show consistent trends in the contamination with iron, and it is this free or freshly added iron that is especially detrimental. The stability of both crude and refined soybean oil would be greatly lowered if most of the iron and copper present in the oil were not complexed.

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.