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Low-Temperature Solvent Fractionation of Animal Fats. Part I. Evaluation of Anhydrous Solvents for Crystallization of White Grease

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THE work reported in this paper is one phase of a broad program directed toward finding new outlets for surplus fats and oils by improving products already available or by preparing new products of greater utility. This phase of the program relates specifically to the fractionation of inedible white grease to produce liquid fractions similar to lard oil, having specific pour points and iodine values and evaluation of methods for such production.

Lard oil has been produced ordinarily from inedible hog fat, known as white grease or yellow grease. It is the more unsaturated, liquid portion of these greases and is more valuable than the raw material because it remains liquid at temperatures normally encountered in its use.

The method used in production of lard oil for many years is the graining and pressing method, in which the grease is cooled slowly for a relatively long period, 3 to 6 days, at about 50°F. It is then placed in bags and pressed to express the lard oil. The slow chilling is necessary to produce a crystal of the type from which the liquid portion will be readily released on pressing. It has been reported (4) that by this method from 50 to 65% of the white grease is expressed as lard oil of 40°F. pour point. The pour point is defined as the temperature, in degrees Fahrenheit, at which the oil will just flow; it is controlled by the temperature to which the grease is chilled and the temperature and care exercised in the pressing. The solid fraction, or stearines, constituting the remainder of the grease, has a higher melting point than the white grease and a lower iodine value but apparently commands no premium over the raw material. The economic success of the process therefore depends on the efficiency with which the yield of the liquid fraction, lard oil, can be held at a high level and the control of its quality. It is apparent that the graining and pressing process has certain disadvantages. Among these are the high labor costs involved in the handling and pressing operations, the high degree of skill required to produce a lard oil of uniform quality from batch to batch, and inability of the process to be run continuously.

Background

The general method of dissolving fats, oils, or fatty acids in various solvents, of cooling these solutions to temperatures at which the higher melting point components become solids, and of separating the solid and liquid phases of the slurries thus formed by filtering has been described by various investigators.

In the laboratory separation of fatty acids and their derivatives Swern (7) and coworkers report on a method employing crystallization from acetone and discuss its applicability to commercial production. Kistler et al. (3) describe "The Commercial Solvent Separation of Fatty Acids," by the Emersol Process, which operates on the principle of controlled crystallization of solid fatty acids from a polar solvent and removal of solid acids by filtration. Methanol of 90% concentration is used. Fractionation of lard and tallow by crystallization from anhydrous acetone on a laboratory scale is described by Riemenschneider et al. (6). Processes have been developed for the fractionation of glycerides by crystallization from various solvents. Among these are propane (4), acetone (2), isopropyl acetate, methyl ethyl ketone, ethyl acetate, ethyl ether, and methyl isobutyl ketone (5).

The need for the solvent evaluation work reported in this paper became apparent in the course of the operation of a low-temperature crystallization pilot plant designed for fractionation of fatty acids, fats, and greases. The process currently under study is the production of oils of improved qualities from commercial greases by controlled crystallization from solvent solutions. Design and cost data are to be developed for the production of the various products made in these operations.

Preliminary work in the pilot plant unit was done with acetone as the solvent, and early tests indicated

that this solvent was satisfactory insofar as it produced easily filterable crystals and good-quality lard oil in high yield. However it was found that relatively low concentrations of water in the solvent, of the order of 2%, decreased the solubility of the white grease to such an extent that fractionation was seriously impaired. The problem of maintaining the water content below this concentration in an operation of commercial size appeared to be important. Since the white grease contained about ½ to 2% water and the operation was carried out at temperatures where condensation of water from the air occurred, concentration of water in the system would be expected to increase as the operation progressed. Even if, at extra cost, equipment were installed to rectify the acetone once every cycle, the varying water concentrations throughout the crystallization and filtration steps would complicate the control of the quality of the product. Solvents such as methyl isobutyl ketone, methyl ethyl ketone, isopropyl acetate, and ethyl acetate, having the property of preferentially dissolving white grease to the exclusion of water in excess of relatively small amounts, were chosen for comparison with acetone, using procedures as follows.

Experimental

A smaller crystallizer of prepilot-plant size, similar to that described by Bailey et al. (1) was constructed so that the tests could be made with relatively small amounts of solvents and grease. Figure 1 shows this equipment. It consisted of a crystallizer tube (A) of 4⅛-inch diameter pipe 10⅛ inches long, cooled by ⅜-inch diameter coils (B) carrying brine, and insulated with 3 inches of hairfelt (C). The scraping device was made up of two blades (D), cut from 0.023-inch thick stainless steel, placed 90° apart on a a hollow, ¾-inch diameter shaft (E) extending to within 1½ inches of the bottom of the crystallizer tube. The scraper shaft was driven by an air motor, through a hydraulic transmission, connected with a V-belt to sheave (F). The speed of the scrapers was controlled during operation by adjustment of the hydraulic transmission. The crystallizer tube was drained through a ⅞-inch hole and pipe (J) in the bottom, which during operation was plugged with a stopper (G) attached to a rod (H) extending through the scraper shaft. After the charge had been crystallized, the stopper was removed by lifting the rod, and the slurry was drained into a chilled filter (K). Temperature was measured with a copper constantan thermocouple (L) extending through the scraper shaft to a point near the bottom of the crystallizer tube; temperatures were recorded on the strip chart of an electronic recorder. The hollow shaft was drilled with a number of ⁷⁄₃₂-inch diameter holes to allow circulation of the slurry past the thermocouple junction.

The slurry was drained from the crystallizer tube to a chilled, 8-inch diameter Buchner funnel fitted with a square-weave duck filter cloth. Filtrations were conducted at 14-inch vacuum, which was maintained constant until a sharp break was seen, indicating fracturing of the cake. Wash solvent was then introduced and vacuum applied until the cake fractured again.

The white grease used in these experiments was a commercial grease of 56 iodine value, 40° C. titer, containing 2.4% free fatty acids and 0.47% water.
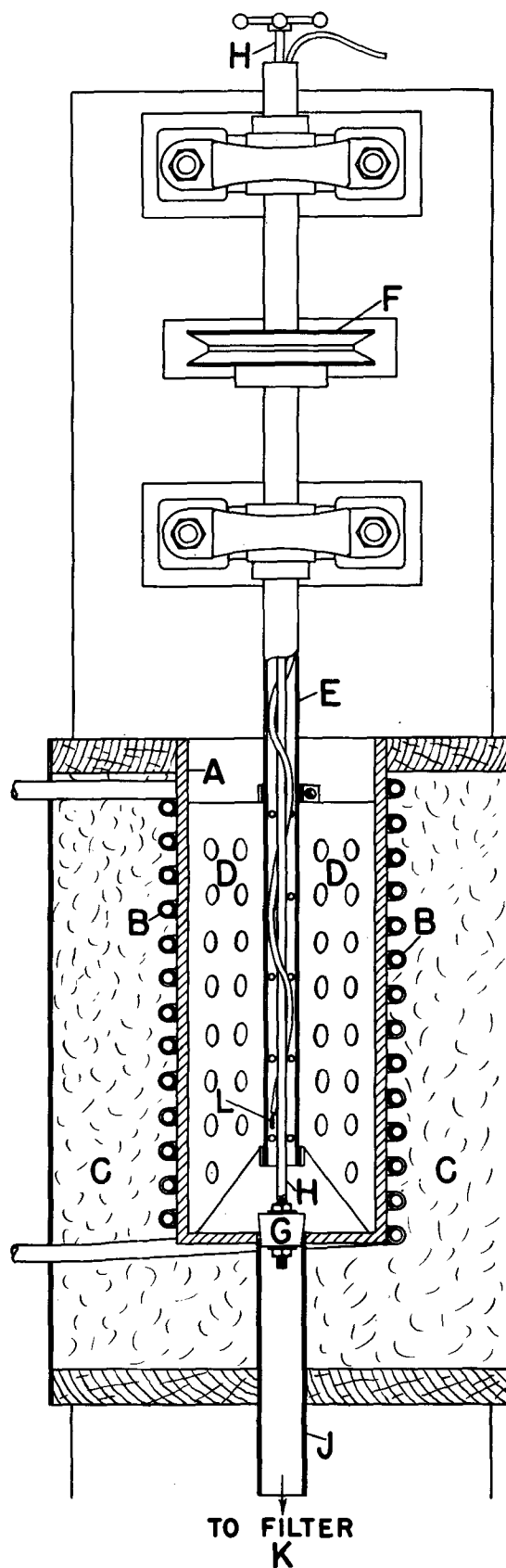

FIG. 1. Prepilot plant size crystallizer.

In order to provide a raw material charge consistent from test to test, sufficient white grease for all tests was melted in a large container, mixed thoroughly, analyzed, and weighed in 300-g. lots into jars, which
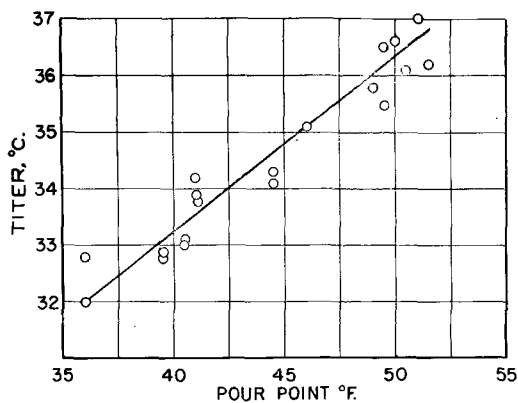
FIG. 2. Titer versus pour point of liquid fractions.

were sealed and stored under refrigeration until used. For each test a crystallizer charge was prepared by melting a 300-g. sample of white grease and dissolving it in 1,500 g. of solvent. The solvent to grease ratio was thus in all cases 5:1 by weight. Charge solutions were introduced into the crystallizer at temperatures between 70 and 80°F. in quantities required to cover the scraper blades. These amounts ranged from 3.4 to 3.9 pounds, depending on the specific gravities of the solvents. After the charge was put in, the scraper was started and maintained at a rate of 10 rpm. This rate was used in all tests reported. Cooling and crystallization were accomplished by circulating brine maintained at a temperature estimated (on the basis of past experience) to give the final crystallization temperature desired. Minor adjustments in brine temperature were made, if necessary, as the crystallizer contents approached the temperature desired. The crystallizer contents were held at the final temperature for a minimum of 40 minutes. The holding time, as shown later, probably was adequate to insure complete crystallization. The filter funnel was precooled by packing it in dry ice; it was set up under the crystallizer, and the slurry was allowed to run in at a rate adjusted to maintain its level about ½ inch below the top of the funnel. The filtrate and wash liquor were collected together in a vacuum flask. A pressure drop of 7.8 psi across the cake and filter cloth, indicated on a manometer, was maintained by adjustment of an air-bleed valve in the vacuum line connected in the filtrate receiver. After all the slurry had been dropped into the filter, filtration was continued until the vacuum could no longer be maintained even by working the surface of the cake to seal the cracks. The wash solvent, precooled to lower-than-crystallization temperature, was then poured on the filter through the crystallizer. Filtration was then continued at the same pressure drop (7.8 psi) until the vacuum could no longer be maintained. Both fractions were weighed. The solid fractions (stearines) were stripped of solvent, and the glycerides analyzed for iodine value. The liquid (lard oil) fractions were stripped of solvent, and the glycerides analyzed for iodine value, titer, °C., and pour point, °F.

In evaluating liquid fractions, the titer rather than the pour point was used as a basis for comparison since it is the more precise of the two determinations. Pour points were determined however on all liquid fractions. They were run in a standard A.S.T.M. pour point tube with an A.S.T.M. pour point ther-

mometer. Two determinations checking within 2°F. were made on each sample. Figure 2 shows the relationship of pour point to titer. Iodine values were determined as an indication of degree of separation of the unsaturated from the saturated glycerides.

Crystallization of commercial white grease from solutions of five solvents was investigated in the temperature range of 20.5 to 49.3°F. The solvents[2] used were acetone, methyl isobutyl ketone, methyl ethyl ketone, isopropyl acetate, and ethyl acetate, all anhydrous. Tests with each solvent were made at four or more crystallization temperatures.

TABLE I

Yield, Titer, and Iodine Value of Liquid and Solid Fractions of White Grease Obtained by Crystallization from Various Solvents

Solvent	Crystallization Temp., °F.	Liquid Triglycerides Fraction				Solid Triglycerides Fraction	
		Yield, % of Charge	Titer °C.	Pour Pt., °F.	Iodine Value	Yield, % of Charge	Iodine Value
Acetone	49.3	74.8	33.9	42	65.6	25.2	26.8
	45	75.1	33	41	65.9	24.9	26.5
	41.7	67.1	32.0	37	68.0	32.9	31.5
	39	87.4	36.1	....	60.0	12.6	16.6
Methyl Ethyl Ketone	36	85.3	36.4	55	62.3	14.7	22.4
	32	75.3	34.3	44	65.4	24.7	30.3
	30.3	74.5	34.1	44	64.5	25.5	28.6
	25	70.2	32.8	37	67.4	29.8	31.3
Methyl Isobutyl Ketone	36	66.7	33.1	....	....	33.3	......
	32	89.0	37	52	60.3	11.0	13.7
	27.7	85.6	36.6	50	61.3	14.4	21.2
	25	79.2	35.1	47	64.3	20.8	24.7
	20.5	74.8	34.2	42	65.2	25.2	27.3
Isopropyl Acetate	35.8	88.0	36.5	49	61.2	12.0	14.9
	32.5	80.0	35.5	49	63.6	20.0	27.4
	27.1	73.3	33.8	42	64.9	26.9	27.1
	24.5	71.3	33.9	35	67.2	28.7	30.0
Ethyl Acetate	36	86.3	36.2	53	61.9	13.7	16.5
	32.5	76.7	34.8	48	63.7	23.3	27.9
	27.5	68.3	32.9	39	66.5	31.7	30.8
	25	68.2	32.8	39	67.7	31.8	29.2

Discussion

Table I shows yield and quality of liquid and solid fractions obtained at the various temperatures. With few exceptions the trends of titer, iodine value, and pour point are as expected. As the crystallization temperature is lowered, more of the saturates are crystallized into the solid fraction, reducing the yield of liquid fraction, lowering its titer and pour point, and increasing its iodine value. Also, as expected, the iodine values of the solid fraction increase as the

[2] Acetone, C. P.; methyl isobutyl ketone, 95%; methyl ethyl ketone, 98%; remaining 2%, sec. butyl alcohol; isopropyl acetate, 95%; remaining 5%, isopropyl alcohol; ethyl acetate, C. P.
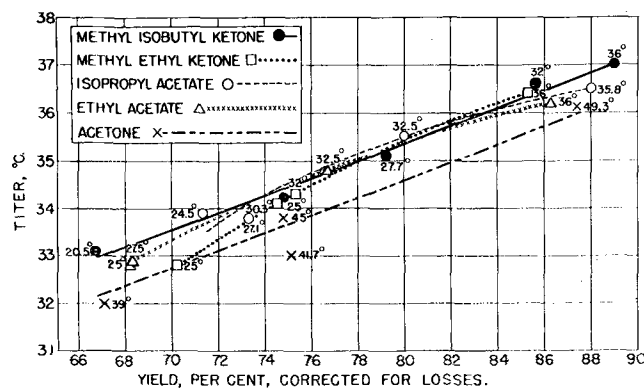

FIG. 3. Yield versus titer of liquid fractions. (Crystallization temperatures indicated.)

TABLE. II

Effect of Holding Time on Yield and Quality of Fractions

Crystallization temperature: 30.3°F.
Solvent: Methyl ethyl ketone
Washing procedure: No washing

Test No.	Holding Time	Solid Fraction		Liquid Fraction						
		Yield	Iodine Value	As Found	Yield Corrected for		Analysis			
					Losses	Losses and Holdup	Iodine Value	Titer °C.	Pour Pt.,°F.	
	min.									
A	15	25.5	33.6	68.4	72.8	78.8	65.1	34.4	46.0	
B	60	29.9	35.9	63.3	67.9	76.0	65.5	33.9	44.0	
C	220	27.6	35.4	63.2	69.6	75.7	66.1	33.7	43.0	

crystallization temperature is lowered since more of the unsaturates also are crystallized into the solid fraction. The yields reported are corrected for mechanical losses by apportioning losses to both fractions on the basis of the weights of the fractions actually recovered. In Figure 3 yields versus titers are plotted for the liquid fractions produced from the various solvents. Crystallization temperatures at which these products were obtained are noted on the curves. These data indicate that, in the range of titers from 32.9° to 36.1°C., liquid fractions of given titer can be prepared by crystallization from a solution of white grease in any of the solvents. In this range of titers material of a given titer can be obtained in varying yield and at varying crystallization temperature, depending on the solvent used. These tests were designed only to compare the solvents. Since all tests were made in the same equipment, with the same cooling rate, scraping rate, and wash procedure, the results may be used with confidence for this purpose. It should be noted however that the yields reported may not represent values obtainable on a commercial or pilot-plant scale. Yields of the liquid fraction are influenced by the holding time at the crystallization temperature, volume of wash solvent employed in cake washing, and temperature of the wash solvent. Some preliminary work was done in evaluating these factors.

Table II shows results of three tests indicating the effect on liquid fraction yield of varying the holding time at crystallization temperature. Each test employed methyl ethyl ketone as the solvent, 30.3°F. crystallization temperature, with no washing of the cake. Time for cooling the slurry from room temperature to final crystallization temperature in these tests was in each case about 2 hours. Yields are reported "as found," "corrected for losses," and "corrected for losses plus holdup." Since the solid fractions were not washed, it was assumed that the solvent held in the cake was associated with liquid triglycerides in the same proportion as in the liquid fraction. Liquid fractions were therefore credited with the liquid triglycerides held in the cake, and the total liquid

glycerides in both fractions were reported as yield "corrected for losses and holdup." In test A, in which a 15-minute holding time was used, a high yield is indicated compared to the other two tests. The high yield, coupled with the higher titer and pour point, indicates incomplete crystallization. Yields at 60 minutes (test B) and 220 minutes (test C) holding time are approximately the same, as are the titers and pour points. From these data it was concluded that the 40-minute minimum holding time used in the tests shown in Figure 3 was probably adequate and that no apparent advantage would be gained by increasing it.

An indication of the effect of amount of wash solvent is recorded in Table III. Data are shown for three tests in which the same solvent (methyl ethyl ketone) and the same crystallization temperature (30.3°F.) were used. Test E, in which 0.422 pound of wash solvent was used, is representative of the method used in determining the results shown in Figure 3. In test D no wash was used, and in test F about double the amount was used as in test E. The yield of liquid fraction is increased with increased wash volume and loss of unsaturates to the solid fraction is reduced, as manifested by the reduced iodine values of the solid fractions. It should be noted also however that liquid fraction iodine values and titers become worse as the wash volume is increased. Because of the solubility of the saturates in the wash solvent some of them are carried into the liquid fraction. In the tests recorded in Table III, as well as in those presented in Figure 3, the temperature of the wash solvent was adjusted to 3 to 5°F. below the crystallization temperature. By lowering the temperatures of the wash solvent however, successive washes may be used without lowering the quality of the liquid fraction. In Table IV a comparison is shown of two tests using methyl ethyl ketone as solvent, a crystallization temperature of 23°F., and three ½-pound washes. Only the temperature of the wash solvent was varied. In the first test (G), in which the wash solvent was used at the higher temperature (6 to 8°F. below the crystallization temperature), the iodine value noticeably decreased as the successive washes were added to the filtrate. The cumulative iodine value was reduced by 1.2 units, from 66.4 to 65.2. When the wash solvent temperature was reduced (test H) (33 to 43°F. below the crystallization temperature), the effect on the liquid fraction iodine value was minimized. The cumulative iodine value was reduced by only 0.2 unit in this case, from 67.7 to 67.5. Information gained from these supplementary tests indicates that the yields shown in Figure 3 are probably lower than the optimum obtainable.

TABLE III

Effect of Volume of Wash Solvent on Yield and Quality of Fractions

Crystallization temperature: 30.3°F.
Solvent: Methyl ethyl ketone

Test No.	Washes	Solid Fraction		Liquid Fraction			
		Yield	Iodine Value	Yield	Iodine Value	Titer °C.	Pour Pt.,°F.
	lbs.						
D	None	32.1	35.9	67.9	65.5	33.9	44.0
E	0.422	25.5	28.6	74.5	64.5	34.1	44.0
F	1.057	21.0	23.4	79.0	63.7	34.5	44.0

TABLE IV
Effect of Temperature of Wash Solvent on Yield and Quality of Fractions

Crystallization temperature: 23°F.
Solvent: Methyl ethyl ketone
Washing procedure: Three ½-lb. washes

Test No.	Wash Temp., °F.	Solid Fraction		Yield Filtr. + Washes	Liquid Fraction + Washes			
		Yield	Iodine Value		Iodine Value			
					Filtr.	+Wash No. 1	+Washes Nos. 1, 2	+Washes Nos. 1, 2, 3
G	+15 to +17	32.0	28.3	68.0	66.4	65.8	65.5	65.2
H	−20 to −10	32.0	28.7	68.0	67.7	67.7	67.6	67.5

Summary and Conclusions

The work thus far completed establishes some of the conditions required for fractionation of white grease by crystallization from five selected solvents. It has been shown that satisfactory fractionation is possible with any of these solvents by controlled crystallization from solutions containing one part of white grease to five parts of solvent by weight. For each solvent the effect of crystallization temperature on the yield and quality of the liquid fraction (as indicated by titer, pour point, and iodine value) has been determined. Preliminary information has been obtained regarding the effects of wash solvent volume, wash solvent temperature, and holding-time at crystallization temperature. These data apply only to water-free solvents. The presence of relatively small amounts of water in acetone, of the order of 2%, reduces its solubility for white grease to such an extent that the grease is separated from the solution as a liquid phase at temperatures above the point where fractionation occurs. The other solvents, methyl ethyl ketone, methyl isobutyl ketone, isopropyl acetate, and ethyl acetate, offer the advantage of separating water in excess of about 2 to 10% while retaining the grease in solution.

Before a choice of solvent can be made for pilot-plant investigation, it is evident that additional research will be required. It is planned to extend the present work in the prepilot-size crystallizer to evaluate the fractionating efficiency, in the white grease process, of these solvents saturated with water. Operations on a larger continuous pilot-plant scale will be required subsequently to determine the final choice of solvent, to obtain data for cost estimates and design, and to prepare quantities of various liquid fractions for commercial evaluation.

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An Improved Procedure for the Purification of Gossypol

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WORKERS in this laboratory, needing to prepare samples of gossypol for use by collaborating laboratories in pharmaceutical and nutritional studies, found the previous methods to be time-consuming, requiring as many as 17 recrystallizations to obtain gossypol of high purity (2-9, 10-13, 15-18, 20-24). An investigation was undertaken therefore to develop a more rapid procedure that would yield gossypol of high purity.

There resulted the improved procedure described herein, which is based on the formation of the gossypol-acetic acid complex, dissociation of the complex in alkaline solution, and recrystallization of gossypol from a mixture of diethyl ether and xylene. This procedure is rapid and yields gossypol of high purity as indicated by the tests of purity whose application is described.

Preparation of Gossypol-Acetic Acid

It was pointed out by Carruth (9) that gossypol in solution in organic solvents combines with acetic acid in the presence of an excess of the acid to form a crystalline compound consisting of one molecule of acid and one of gossypol.

Gossypol was recovered as gossypol-acetic acid from portions of the butanone extract of cottonseed flakes which were used in preparing 3,000 lb. of cottonseed meal for nutritional investigations.[2] The concentrated extracts, obtained from 85-lb. batches of cottonseed flakes, were filtered and the volume reduced to 1,750 ml. by evaporation under vacuum in the laboratory. The crude acetic acid complex, precipitated by the addition of 850 ml. of glacial acetic acid, was allowed

[2] Oil-free (hexane-extracted) flakes were re-extracted with butanone in a batch extractor by the Engineering and Development Division (19). When the system was operated under atmospheric pressure, much of the gossypol was decomposed; but at low temperatures, under reduced pressure, recovery was satisfactory. Approximately 39% of the gossypol in the flakes was extracted in 4 hours.