Low-Temperature Solvent Fractionation of Animal Fats. II. Evaluation of Water-Saturated Solvents for Crystallization of White Grease

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PREVIOUSLY reported work of this laboratory (2) evaluated certain anhydrous solvents for the fractionation of white grease by low-temperature crystallization to produce lard oil. That work established some of the conditions required for fractionation of white grease from solutions in acetone, methyl isobutyl ketone, methyl ethyl ketone, isopropyl acetate, and ethyl acetate. It was 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) was determined.

It was found that acetone, which appeared to be the best solvent when anhydrous, did not retain the white grease in solution when small amounts of water were present. Since commercial white grease contains small amounts of water and the process involves filtration at temperatures where condensation of water from the air occurs, acetone was eliminated as not meriting further investigation. The other solvents however, because of their limited solubility for water, automatically control the water concentration of the system by separating excess water out of solution for convenient decantation.

Continuing the work previously reported on evaluation of anhydrous solvents, this paper presents similar data for the same solvents saturated with water.

Experimental

A small crystallizer similar to that described by Bailey *et al.* (1) was used so that the tests could be made with relatively small amounts of solvent and grease. This equipment was described in detail in an earlier paper (2). It consisted of a vertical pipe 4⅛ in. in diameter and 10⅛ in. long, wrapped on the outer surface with ⅜-in. diameter coils carrying brine for cooling, and fitted with a device for continuously scraping the inner surface. Filtrations were made on a chilled 8-in. diameter Buchner funnel fitted with a square weave duck filter cloth.

A commercial white grease was used in these experiments, having a 56 iodine value and 40°C. titer and containing 2.4% free fatty acids and 0.47% water. 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, and weighed in 300-g. lots into jars, which were sealed and refrigerated until used. Solvents were saturated with water at room temperature by shaking with an excess of water, allowing the excess to separate, and decanting. 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 the solvent. The solvent-to-grease ratio was thus in all cases 5:1 by weight, "solvent" being defined as the commercial solvent plus enough water to saturate it. Charge solutions, introduced into the crystallizer at temperatures between 70 and 80°F. in quantities required to cover the scraper blades, ranged in amounts from 1,500 to 1,650 g., depending on the specific gravities of the solvent. After the charge was put in, the scraper was started and maintained at a rate of 10 r.p.m. Cooling and crystallizing were controlled by circulating brine held at a temperature estimated to give the final crystallization temperature required. As the crystallizer contents approached the temperature desired, minor adjustments in brine temperature were made if necessary. To insure complete crystallization the crystallizer contents were held at the final temperature for a minimum of one hour. The filter funnel, precooled in dry ice, 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 (vacuum of 14″ Hg.), indicated on a manometer, was maintained by adjustment of an air bleed valve in the vacuum line connected to the filtrate receiver. Filtration was continued until the vacuum could no longer be maintained even by working the surface of the cake to seal the cracks. Wash solvent was saturated with water at room temperature, cooled to a point about 5°F. below that of the final wash temperature, and filtered to remove ice crystals. Washes were used at a temperature low enough to prevent any solution of the cake, or about 40°F. below the crystallization temperature. A first wash of ½ lb. was poured through the crystallizer onto the cake in the filter funnel. Second and third washes each of ½ lb. were poured directly on the cake. A suitable interval was allowed between washes to permit removal of most of the previous wash from the cake. After the final third wash the cake was dried until the vacuum could no longer be maintained. Both fractions were weighed, and the concentrations of glycerides and water in each fraction were determined. The glycerides obtained from the cake were analyzed for iodine value, those obtained from the filtrate were analyzed for iodine value, titer, and pour point. Fractions were not analyzed as a routine for free fatty acid content. On one series of tests however (see Table I, methyl ethyl ketone, anhydrous) these analyses were made and indicated that about 98% of the free fatty acids in the glycerides charged were recovered in the lard oil fraction.

TABLE I

Yield and Constants of Fractions Crystallized from Various Solvents

Solvent	Crystallization Temp., °F.	Liquid Triglycerides Fraction					Solid Triglycerides Fraction		
		Yield, % of Charge	Titer, °C.	Pour Point, °F.	Iodine Value	Water Content[a]	Yield, % of Charge	Iodine Value	Water Content[a]
Methyl ethyl ketone (water 11.9%)	49.1	87.8	36.1	51	59.4	98.2[b]	12.2	16.1	1.8
	40.0	75.2	33.8	41	63.0	.....	24.8	25.4	.....
	34.7	64.5	31.7	37	67.1	95.8[b]	35.5	33.3	4.2
	26.8	60.3	30.9	30	69.1	96.3[b]	39.7	32.9	3.7
Methyl iso butyl ketone (water 1.7%)	36.0	89.6	36.8	51	60.6	70.2[c]	10.4	11.9	29.8[c]
	31.7	86.4	36.0	48	61.5	94.6	13.6	16.6	5.4
	28.2	81.6	34.7	46	63.5	91.0	18.4	21.1	9.0
	23.8	76.2	33.4	43	65.2	71.0	23.8	24.7	29.0
Isopropyl acetate (water 2.3%)	35.2	86.4	35.8	50	62.0	78.5	13.6	16.5	21.5
	31.4	80.0	34.3	45	63.2	79.5	20.0	21.8	20.5
	27.8	75.6	33.2	42	64.3	70.4	24.4	24.9	29.6
	24.7	73.3	32.7	39	64.6	67.1	26.7	25.9	32.9
Ethyl acetate (water 2.8%)	39.9	88.2	35.9	49	59.7	90.9	11.8	14.6	9.1
	36.0	83.3	34.8	....	60.4	82.1	16.7	20.0	17.9
	31.7	77.0	33.8	42	62.5	74.2	23.0	24.1	25.8
	28.0	72.6	32.9	39	65.8	65.4	27.4	26.8	34.6
						Free fatty acids, %[d]			Free fatty acids, %[d]
Methyl ethyl ketone (anhydrous)	35.8	88.8	36.2	51	59.2	99.37	11.2	13.4	0.63
	32.5	83.1	34.8	48	63.2	98.80	16.9	20.9	1.20
	27.8	77.8	33.7	43	64.0	97.99	22.2	24.2	2.01
	25.0	75.3	32.7	40	64.0	.....	24.7	25.8	.....

[a] % of water in charge recovered in fraction corrected for losses.
[b] Includes amount in small layer (76% water) which separated from filtrate.
[c] Wash solvent not filtered to remove ice crystals.
[d] % of free fatty acids in charge recovered in fraction corrected for losses.

Crystallization of the white grease from solutions in four solvents,[3] methyl ethyl ketone, methyl isobutyl ketone, isopropyl acetate, and ethyl acetate all water-saturated, was conducted in the temperature range of 24 to 49°F. Tests with each solvent were made at four crystallization temperatures.

Discussion

Yield and quality of liquid and solid fractions obtained at various crystallization temperatures are shown in Table I. In all cases with a lowering of crystallization temperature, liquid fraction yields, titers, and pour points are lowered and iodine values increased since more of the higher freezing point stearins of low iodine value are removed. With a lowering of crystallization temperature however more unsaturates are lost to the solid fraction as indicated by its increasing iodine value. Also as the crystallization temperature is lowered, the amount of water recovered in the solid fraction is increased. 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. Figure 1 shows yields *vs.* titers for the liquid fractions produced from the various water-saturated solvents.

[3] Methyl ethyl ketone, 98%; methyl isobutyl ketone, 95%; isopropyl acetate, 95%; ethyl acetate, 99%.

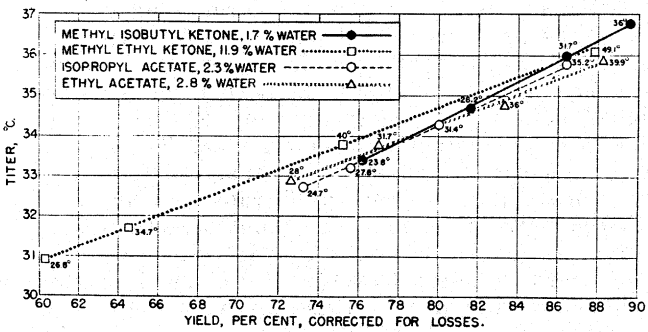

FIG. 1. Yield *vs.* titer of liquid fractions. (Crystallization temperatures indicated.)

Rating the water-saturated solvents solely on the basis of the crystallization temperature required to produce a given titer lard oil, points of constant titer can be chosen and, from Figure 1, crystallization temperatures and yields can be read for each solvent. This method was used in preparing Table II. Rated solely on the basis of the crystallization temperature required to produce a given titer oil, it is apparent from Table II that methyl ethyl ketone is best. Ethyl acetate, isopropyl acetate, and methyl isobutyl ketone are progressively poorer in that order.

TABLE II

Crystallization Temperatures Required to Produce Lard Oils of Specific Titer from Water-Saturated Solvents

Solvent	% Water in Saturated Solv.-Water Solution	Titer 33.5°C.		Titer 34.0°C.		Titer 35.0°C.	
		Crys. Temp., °F.	Yield, %	Crys. Temp., °F.	Yield, %	Crys. Temp., °F.	Yield, %
M.E.K.	11.9	39.3	73.8	40.9	76.4	44.6	81.6
Et. Ac.	2.8	30.6	75.8	32.7	78.5	36.2	83.6
Isop. Ac.	2.3	28.7	76.7	30.4	78.9	33.3	83.2
M.I.K.	1.7	24.2	76.7	25.8	78.6	29.0	82.6

Rating the anhydrous solvents by the same procedure from previously published curves (2), Table III is obtained. On the basis of crystallization temperature, from Table III, the anhydrous solvents would be rated in the order listed. The order of rating is the same as for the water-saturated solvents in Table II. Comparing crystallization temperatures for each solvent, anhydrous against water-saturated, it is shown that the water-saturated solvents permit the use of significantly higher crystallization temperatures for the same titer. It appears that the increase in crystallization temperature is related to the solubility of water in the glycerides-solvent-water system. In the case of M.E.K., where the water concentration is highest (11.9%), the increase in crystallization temperature is about 11°F. In the cases of the other solvents, where the water concentration is appreciably lower, smaller increases in crystallization temperatures are noted: Et. Ac., 2.8% water, 3.2°F. increase;

TABLE III

Crystallization Temperatures Required to Produce Lard Oils of Specific Titer from Anhydrous Solvents

Solvent	Titer 33.5°C.		Titer 34.0°C.		Titer 35.0°C.	
	Crys. Temp., °F.	Yield, %	Crys. Temp., °F.	Yield, %	Crys. Temp., °F.	Yield, %
M.E.K.	28.2	72.5	29.6	74.3	33.2	78.4
Et. Ac.	27.3	70.7	29.6	72.8	32.9	77.9
Isop. Ac.	24.0	70.9	25.4	72.8	30.2	77.2
M.I.K.	22.2	69.8	23.7	72.4	27.0	77.9

Isop. Ac., 2.3% water, 4.2°F. increase; and M.I.K., 1.7% water, 2°F. increase.

It should be mentioned that the yields shown in Table II may not be compared directly with the yields in Table III for the reason that different wash procedures were used. In the tests on water-saturated solvents (Table II) three washes were used, and in the tests on anhydrous solvents (Table III) only one wash was used. Earlier work (2) has shown that lard oil yields are augmented by increasing the number of washes but that titers are not changed appreciably, provided the wash solvent temperature is maintained (as it was in both series of tests) about 30 to 40°F. lower than the crystallization temperature. In order that a direct comparison of yield as well as crystallization temperature can be made for an anhydrous solvent against the same solvent, water-saturated, a series of tests was made, using anhydrous M.E.K. In this series three ½-lb. washes were used, exactly as used in the M.E.K. water saturated series. Figure 2 shows yields *vs.* titers for M.E.K. anhydrous and M.E.K. water-saturated, obtained under comparable test conditions. Crystallization temperatures are shown on the curves.

Table IV was compiled by choosing points of constant titer and reading from the curves of Figure 2 yields and crystallization temperatures. These data indicate that the same titer oil can be made at a crystallization temperature about 12°F. higher from water-saturated M.E.K. than from the same solvent, anhydrous. The yields of oil obtained are nearly the same for both solvents at the higher titers, but the difference increases in favor of the anhydrous solvent at the lower titers, differing by 4.8% at the lowest titer compared.

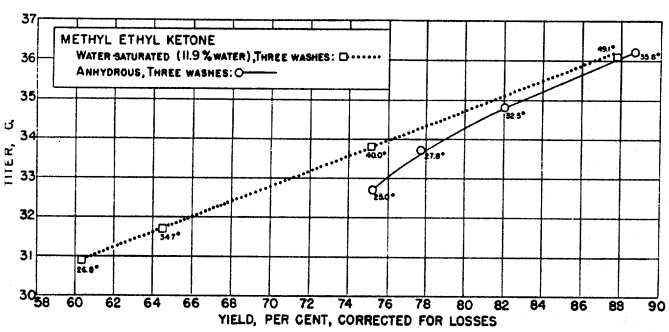

FIG. 2. Yield *vs.* titer of liquid fractions. Methyl ethyl ketone anhydrous and water-saturated. (Crystallization temperatures indicated.)

TABLE IV

Comparison of Crystallization Temperatures Required and Lard Oil Yields Obtained in Producing Specific Titer Oils from M.E.K. Anhydrous and Water-Saturated

Lard Oil Titer, °C.	Yield, %		Crystallization Temperature, °F.		Crys. Temp. Difference, °F.
	Anhydrous Solvent	Water-Satd. Solv.	Anhydrous Solvent	Water-Satd. Solv.	
36.0	87.7	86.7	35.4	48.3	12.9
35.5	85.3	84.1	34.3	46.5	12.2
35.0	83.0	81.5	33.2	44.6	11.4
34.5	80.8	79.0	31.0	42.7	11.7
34.0	79.0	76.4	29.0	40.8	11.8
33.5	77.4	73.8	27.3	39.3	12.0
33.0	76.0	71.2	25.8	38.0	12.2

Filterability of the slurries was not determined quantitatively. It was observed however that the time required to filter a slurry of a given solids content did not vary appreciably for the same solvent whether anhydrous or water-saturated.

Summary and Conclusions

This work establishes some of the conditions required for the fractionation of white grease by crystallization from four selected water-saturated solvents. The effect of crystallization temperature on yield and constants of the liquid and solid fractions obtained by crystallization has been determined. A comparison of these data with previously published data on the same solvents, anhydrous, indicates that appreciably higher crystallization temperatures are permissible with water-saturated solvents than with the same anhydrous solvents. The comparison also indicates that the solvent (methyl ethyl ketone) having the highest solubility for water shows the greatest increase in crystallization temperature for production of a given titer oil.

Methyl ethyl ketone, when used water-saturated, produced the same titer oil at a 12°F. higher crystallization temperature than when it was used anhydrous. The yields of lard oil obtained from the water-saturated solvent however were measurably lower than from the anhydrous solvent.

It is concluded from this work that some economic advantage may be gained by using water-saturated solvents in that the higher crystallization temperatures represent a saving in refrigeration costs. However this must be measured against the lowering of yield. The use of the solvents having a limited solubility for water assures a constant water content of the system since water in excess of that soluble in the grease-solvent solutions separates and can be decanted. Such a system may be more easily and closely controlled than one in which the water content varies, as would be the case using a solvent having an unlimited solubility for water, since crystallization temperature requirements vary not only with the solvent but with its water content.

Continuous pilot-plant tests are planned to provide, as these tests have not, data on solvent losses and other engineering data required for cost estimation and design and to prepare quantities of liquid fractions for commercial evaluation.

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