Low-Temperature Solvent Crystallization of Soybean Oil and Soybean Oil Fatty Acids

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Introduction

The use of crystallization to separate fats, oils or fatty acids into high-melting saturated fractions and low-melting unsaturated fractions is used in only a few processes commercially at the present time. Cottonseed oil is often "winterized" by cooling and pressing to remove higher melting glycerides and thus make the oil stable against freezing at ice-box temperatures. Soybean oil solidifies at a lower temperature and does not require "winterizing," although this process is sometimes used to remove traces of waxes which are present. The pressing of stearin and stearic acid are other examples. Apparently, such a separation has not been applied to the semidrying oils in order to obtain fractions with improved drying properties.

Hilditch (1) has used low-temperature crystallization of solid fats and some liquid seed oils as a step in studying glyceride composition. J. B. Brown (2) has reviewed much of the work which has been done on low-temperature crystallization of fats and fatty acids. Baldwin (3) has shown that crystallization of fish oil (iodine number 181.5) from acetone afforded a 12.5 percent yield of filtrate material with an iodine number of 264. Riemenschneider (4) used low temperature crystallization from acetone on cottonseed oil (iodine number 108) to obtain fractions with iodine numbers varying from 52.5 to 148.3, the latter fraction representing a 4.8 percent yield of the original oil.

The present work was undertaken to determine how effectively soybean oil could be crystallized from a solvent at low temperatures to produce high and low iodine number fractions. The high iodine number fractions should be more valuable in the drying oil field and the low iodine number fractions should be more suitable for food purposes. Most of the data determined are concerned with the degree of separation possible by a single crystallization, as affected by solvent, solvent-ratio and temperature. It was thought that such data on a single crystallization would be most useful in evaluating the possible commercial application of low temperature solvent crystallization of soybean oil. Because of the mixed nature of the natural glycerides in soybean oil, it was to be expected that separation would be less effective on the oil than on the mixed acids. Some crystallization data are presented for the mixed acids of soybean oil to show this comparison.

Experimental

Crystallization of Oil. Preliminary attempts to crystallize the oil without solvent resulted in poor separation and very difficult filtration, indicating that a practical separation would require the use of solvents. Qualitative observations were made on 35 different solvents at —15°, —30°, and —40° C., using solvent ratios of 1, 2.5, 5, and 10. ("Solvent ratio" refers to cc. of solvent per gram of oil.) Acetone and methyl acetate were found to be most suitable with regard to crystal formation. Quantitative tests showed acetone to be superior to methyl acetate, and the former solvent was therefore used in this study.

The cooling of the samples was done in a thermostatically controlled low-temperature bath which used solid carbon dioxide as the cooling material. The bath could be controlled to within ± .3° C. and had a range from room temperature to —70°C.

For the quantitative data, 5 grams of oil were weighed into a large test tube, the solvent was added, and the mixture was placed in the bath. After crystallization was complete, filtration was made by means of a filter stick which had been previously cooled to bath temperature. In most cases, the samples were placed in the bath at room temperature and cooled to the desired temperature over a period of ½ to 2 hours, depending upon the temperature to be obtained. Tests on several samples showed that practically the same results as regards yields and iodine numbers of solid and liquid fractions were obtained if the sample was cooled rapidly by placing it directly in the bath at the desired temperature. However, rapid cooling sometimes caused the precipitate to filter with difficulty. Slower cooling also made it possible to observe the temperature at which the oil first started to come out of solution. The samples were ordinarily held at crystallization temperature for one hour before filtering, but tests showed that periods from ½ to 4 hours made very little difference as to yield and iodine number of the fractions obtained. Unexpectedly, in several cases longer crystallization periods made filtration more difficult.

Preliminary determinations made with low solvent ratios at relatively high temperatures showed that higher solvent ratios and lower temperatures were necessary for the best separation.

Because of certain references to the necessity of avoiding water in acetone used for crystallizations, tests were made to determine the effect of adding 1 percent by volume of water. Instead of adverse effects, the crystallization from acetone containing 1 percent of water had some advantages. In many cases, filtration was more rapid than when anhydrous acetone was used and showed less effect of cooling rate, although the precipitates from acetone plus 1 percent of water often did not appear as crystalline as those from anhydrous acetone. The addition of the 1 percent of water raised the temperature at which oil first separated from the solution, and also raised the temperature at which a given percent of

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TABLE I.

Crystallization of Alkali Refined Soybean Oil (Iodine No. 132.5) from Acetone

Temp. °C.	Solvent Ratio	Filtrate Material			Precipitate			
		Actual Yield	Corrected Yield	I. No.	Actual Yield	Actual I. No.	Corrected Yield	Corrected I. No.
		Percent	*Percent*		*Percent*		*Percent*	
—15	2.5	46.0	52.0	137.0	54.0	128.8	48.0	127.8
	5	48.0	60.0	136.9	52.0	124.4	40.0	120.6
	10	66.0	94.0	134.9	34.0	126.4	6.0	86.7
	20	88.0	98.0	135.0	12.0	116.0	2.0	27.0
—30	2.5	16.0	23.0	147.5	84.0	130.5	77.0	129.0
	5	28.0	31.0	146.6	72.0	127.4	69.0	126.6
	10	42.0	55.0	145.7	58.0	124.0	45.0	117.7
	20	68.0	90.0	139.9	32.0	118.6	10.0	71.7
—40	5	17.0	19.0	152.7	83.0	126.7	81.0	126.0
	10	36.0	41.0	150.7	64.0	121.8	59.0	119.4
	20	62.0	68.0	146.6	38.0	108.3	32.0	101.1
	30	76.0	84.0	142.3	24.0	104.3	16.0	85.3
	40	72.0	82.0	141.6	28.0	106.0	18.0	86.2
—45	10	30.0	32.0	156.5	70.0	120.0	68.0	118.9
	20	46.0	58.0	153.4	54.0	115.0	42.0	104.1
—47.5	10	4.0	5.0	163.0	96.0	131.2	95.0	130.9
	20	6.0	7.0	161.2	94.0	130.3	93.0	130.0
—50	10	2.0	2.0	157.0	98.0	132.0	98.0	132.0
	20	2.0	2.0	155.0	98.0	131.5	98.0	131.5
—70	20	2.0	2.0	153.8	98.0	131.3	98.0	131.3

oil would appear in the filtrate. However, a greater solvent ratio was required to obtain an equally efficient separation with regard to iodine number and yield of the fractions.

As the temperature was lowered, the difference between acetone and acetone plus 1 percent of water became less, until at —50° the result was essentially the same with either solvent; namely, a 2 percent yield was obtained in the filtrate. The yield of oil in the filtrate decreased very suddenly below —45°. Thus, with a solvent ratio of 10, the yield in filtrate was 32 percent at —45° and 5 percent at —47.5°, while with a solvent ratio of 20, the yield was 58 percent at —45° and 7 percent at —47.5°. Obviously very small temperature differences in this range would cause large effects on yields, and this fact undoubtedly accounts for some of the anomalous results obtained in this temperature range.

Table I shows the yields and iodine numbers of the precipitates and filtrates obtained with acetone at various crystallization temperatures. Table II shows the same data for acetone plus 1 percent of water. The oil used was an alkali refined soybean oil with an iodine number of 132.5 (Wijs, ½ hour).

The precipitate was always more or less contaminated with occluded mother liquor. It was assumed that this retained mother liquor had the same composition as the filtrate, and consequently its quantity could be estimated by determining the amount of acetone present in the precipitate. From the determined ratio of acetone to oil in the filtrate, and from the determined iodine number of the oil recovered from the filtrate, appropriate corrections of yields and iodine numbers of precipitate material and corrected yields of filtrate material were calculated and are reported in Table I as corrected values. Figure 1 shows yield (corrected) and iodine number of filtrate as related to crystallization temperature.

Several significant facts are revealed by these data. The efficiency of separation is increased with increasing solvent ratio up to a ratio of 20 to 1 with acetone, and up to a ratio of 30 to 1 with acetone plus 1 percent of water. With the higher ratios, the iodine number of filtrate material increases rather rapidly with decreased yield to an iodine number of 150 to 155 at 40 to 50 percent yield. When the yield of filtrate material is further reduced by the use of lower temperatures, the iodine number increases only very slightly, and tends to level off at a value of 155 to 160. This may be due in part to concentration of unsaponifiable material in the filtrates, since a crystallization at —60°, with a 20 to 1 ratio, afforded 1.4 percent of filtrate material containing 27 percent unsaponifiable matter. This effect also probably accounts for the fact that the precipitates showed refractive indices in good agreement with the iodine number, while the low-yield filtrates always showed a refractive index much higher than would be normal for the observed iodine number (5).

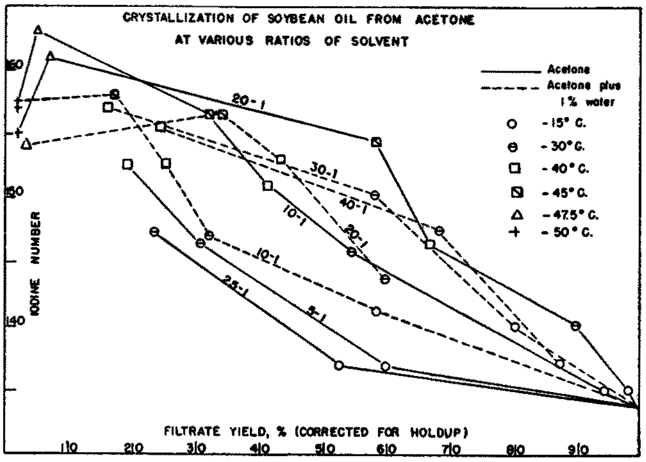

FIG. 1.

A sample of filtrate material with an iodine number of 152 was compared with raw linseed oil and non-break soybean oil in paints of identical formulation. The non-break soybean oil paint dried in 10½ hours, that from the unsaturated fraction in 7 hours, and that from raw linseed in 5½ hours, as determined on the Sanderson drier.

Crystallization at —70° gave essentially the same result as at —50°, namely 2 to 3 percent yield in the filtrate with an iodine number around 154. Also, whenever the yield in filtrate was lowered to 2 or 3 percent, regardless of solvent or ratio, the filtrate material was solid at room temperature and had an iodine number of 155 to 160. This material was further investigated by preparing a larger amount, using a ratio of 20 to 1 at —60°. The filtrate material was recrystallized from acetone at —40° and washed with cold petroleum ether. A white crystalline material, melting at 134-7° C., was obtained in a yield of 0.15 percent of the original oil. It gave a strong Liebermann-Burchard sterol test, and appeared similar to the mixed sterols of soybean oil described by Kraybill (6). This may be a convenient laboratory method of separating sterols from vegetable oils. The coloring materials in the oil also concentrated in the filtrates.

Recrystallization of high and low iodine number fractions was carried out to determine the extent to which these fractions could be further separated, but the results on the high iodine number filtrate fraction were not very encouraging. The starting material was obtained by crystallizing 500 grams of oil at —40° from acetone plus 1 percent of water with a solvent ratio of 20 to 1. The iodine number of the precipitate material was 118 and that of the filtrate material, 152. The filtrate material was crystallized at lower temperatures from acetone and acetone plus 1 percent of water with the same and higher solvent ratios. The crystallization temperature range was very short, indicating that temperature was a critical factor. Even with very high solvent ratio, separation was not very good. The effect of unsaponifiable matter is of course further increased in these filtrates. The results are shown in Table III. Only very small yields of oil above 160 in iodine number were obtained.

The precipitate material from the original —40° crystallization (iodine number 118) was recrystallized under various conditions with the results shown in Table IV.

Crystallization of Acids. The mixed fatty acids (iodine number 137.2) were prepared from some of the same oil as used in the above mentioned work and were crystallized from acetone at various ratios of solvent at a number of temperatures. As would be expected, the separation was much more efficient than with the oil. Table V and Figure 2 to show these results.

As was the case with the oil, higher solvent ratios gave better separation, but the effect was not generally as great as with oil. In Figure 2, the numbers beside the points refer to solvent ratios and only the points for the 40 to 1 solvent ratio are connected. It will be seen that filtrate material yields of 40 to

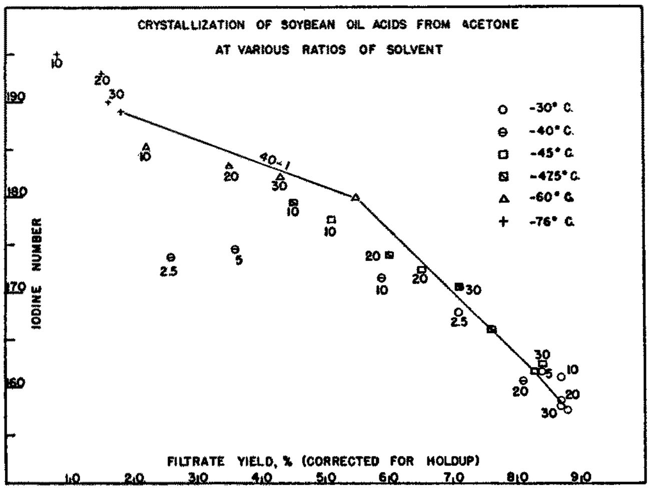

FIG. 2.

TABLE II.

Crystallization of Alkali Refined Soybean Oil (I. No. 132.5) From Acetone Plus 1 Percent of Water

Temp. °C.	Solvent Ratio	Filtrate Material			Precipitate			
		Actual Yield	Corrected Yield	I. No.	Actual Yield	Actual I. No.	Corrected Yield	Corrected I. No.
		Percent	*Percent*		*Percent*		*Percent*	
—15	10	56.0	58.0	141.2	44.0	125.6	42.0	124.8
	20	85.0	95.0	136.2	15.0	114.3	5.0	70.5
	30	87.0	92.0	136.0	13.0	102.8	8.0	82.0
	40	96.0	98.0	135.6	4.0	91.2	2.0	47.8
—30	10	30.0	32.0	147.0	70.0	125.0	68.0	124.4
	20	56.0	60.0	143.7	44.0	118.9	40.0	116.4
	30	76.0	80.0	139.8	24.0	106.4	20.0	99.7
	40	84.0	88.0	136.8	16.0	96.9	12.0	83.6
—40	10	24.0	25.0	152.7	76.0	127.0	75.0	126.6
	20	40.0	43.0	152.0	60.0	120.8	57.0	119.2
	30	50.0	58.0	150.3	50.0	113.6	42.0	106.6
	40	60.0	68.0	147.5	40.0	107.6	32.0	97.6
—45	10	16.0	17.0	158.4	84.0	126.4	83.0	126.0
	20	32.0	34.0	156.5	68.0	120.2	66.0	119.1
	30	14.0	16.0	157.0	86.0	127.1	84.0	126.4
	40	22.0	24.0	155.7	78.0	123.8	76.0	123.0
—47.5	10	8.0	9.0	155.4	92.0	129.5	91.0	129.2
	20	4.0	5.0	157.8	96.0	130.7	95.0	130.4
	30	5.0	5.0	158.1	95.0	129.6	95.0	129.6
	40	8.0	8.0	152.0	92.0	129.5	92.0	129.5
—50	10	2.0	2.0	157.8	98.0	131.8	98.0	131.8
	20	3.0	3.0	154.0	97.0	131.1	97.0	131.1
—70	20	2.0	2.0	153.7	98.0	131.8	98.0	131.8

50 percent with an iodine number of 175 to 180 were obtained at —45° to —47.5° with a solvent ratio of 10 to 1. It is interesting to note that in crystallization of the acids, the iodine number does not tend to level off or decrease when lower yields are obtained, as was the case with the oil. This is not readily explainable, since the unsaponifiable matter is presumably present in the acids as well as in the oil from which they were prepared. Apparently, the separation of the acids is so much more efficient that any effect of unsaponifiable matter is not sufficient to have a very great effect at the yields obtained.

Summary

1. A study has been made of the separation of soybean oil and soybean oil acids into saturated and unsaturated fractions by low temperature solvent crystallization, using acetone and acetone plus 1 percent of water, at solvent ratios of 2.5 to 40, at temperatures from —15 to —76°C.

2. Crystallization from higher ratios of solvent at correspondingly lower temperatures gave the most efficient separation with regard to iodine number for a given yield.

3. Yields of 30 to 60 percent of unsaturated fractions with iodine numbers of 145 to 155 have been obtained from oil having an iodine number of 132.5 in a single crystallization by suitable choice of solvent ratio and temperature.

4. By a single crystallization, it was impossible to obtain an unsaturated fraction with iodine number above 165, even at low yields of unsaturated fractions.

5. At —50° and below only 2 percent yields were obtained in the filtrate. This fraction was high in unsaponifiable and could be crystallized at —40°C. to afford crude sterols in a yield of 0.15 percent of original oil.

6. Crystallization of the unsaturated fraction at temperatures lower than used for the original separation afforded material with an iodine number as high as 166 in low yields.

7. Recrystallization of saturated fraction at a temperature higher than used for the original separation

TABLE III.

Crystallization of —40° Filtrate Material (I. No. 152)

Temp. °C.	Solvent Ratio	Percent Added Water	Filtrate Material			Precipitate			
			Actual Yield	Corrected Yield	I. No.	Actual Yield	Actual I. No.	Corrected Yield	Corrected I. No.
			Percent	*Percent*		*Percent*		*Percent*	
—47.5	40	1	9.0	9.0	164.3	91.0	152.2	91.0	152.5
	50	1	17.0	17.0	165.7	83.0	150.5	83.0	150.5
	60	1	82.0	82.0	156.7	18.0	137.5	18.0	137.5
—50	20	0	7.0	8.0	162.5	93.0	152.4	92.0	152.3
	30	0	7.0	8.0	166.1	93.0	151.7	92.0	151.5
	40	0	62.0	63.0	156.6	38.0	146.8	37.0	146.6
	40	1	7.0	7.0	163.1	93.0	152.7	93.0	152.7
	50	0	77.0	78.0	155.6	23.0	143.5	22.0	142.9
	50	1	7.0	7.0	166.0	93.0	152.6	93.0	152.6
	60	1	8.0	8.0	166.1	92.0	152.1	92.0	152.1
—51	30	0	8.0	8.0	167.7	92.0	152.8	92.0	152.8
	35	0	66.0	67.0	157.7	34.0	146.3	33.0	145.4
	40	0	57.0	57.0	157.0	43.0	149.0	43.0	149.0
	50	0	84.0	84.0	156.3	16.0	137.7	16.0	137.7
—52.5	30	0	5.0	6.0	160.8	95.0	151.6	94.0	151.6
	35	0	6.0	6.0	162.1	94.0	149.1	94.0	149.1
	40	0	9.0	9.0	164.7	91.0	147.7	91.0	147.7
	50	0	8.0	8.0	164.3	92.0	146.7	92.0	146.7

TABLE IV.

Recrystallization of —40° Precipitate (I. No. 118)

Temp. °C.	Solvent Ratio	Percent Water Added	Filtrate Material			Precipitate			
			Actual Yield	Corrected Yield	I. No.	Actual Yield	Actual I. No.	Corrected Yield	Corrected I. No.
			Percent	*Percent*		*Percent*		*Percent*	
—10	20	2	72.0	76.0	126.1	28.0	106.1	24.0	102.9
	30	2	82.0	92.0	123.9	18.0	102.1	8.0	70.9
	40	2	77.0	80.0	123.7	23.0	84.7	20.0	61.3
	30	3	64.0	67.0	127.3	36.0	106.4	33.0	104.3
—12.5	20	2	66.0	67.0	126.8	34.0	106.1	33.0	105.5
	30	2	84.0	90.0	124.6	16.0	95.3	10.0	79.3
	40	2	84.0	90.0	123.9	16.0	92.5	10.0	65.6
—15	20	1	73.0	84.0	123.8	27.0	105.7	16.0	80.9
	30	1	83.0	92.0	124.8	17.0	96.7	8.0	65.0
	40	1	81.0	92.0	124.2	19.0	100.3	8.0	67.5
	40	2	84.0	89.0	124.7	16.0	89.1	11.0	70.9
—20	20	2	47.0	48.0	123.6	53.0	106.4	52.0	106.1
	20	3	31.0	32.0	132.2	69.0	110.6	68.0	110.3
—25	20	2	38.0	41.0	132.8	62.0	107.8	59.0	106.6
	20	3	26.0	27.0	135.7	74.0	111.5	73.0	111.1
—40	20	0	64.0	73.0	144.0	36.0	105.6	27.0	90.1

TABLE V.

Crystallization of Mixed Fatty Acids (I. No. 137.2) from Acetone

Temp. °C.	Solvent Ratio	Filtrate Material			Precipitate			
		Actual Yield	Corrected Yield	I. No.	Actual Yield	Actual I. No.	Corrected Yield	Corrected I. No.
		Percent	*Percent*		*Percent*		*Percent*	
—30	2.5	27.0	71.0	167.8	73.0	124.1	29.0	55.4
	5	63.0	84.0	161.6	37.0	96.3	16.0	10.6
	10	80.0	87.0	161.0	20.0	52.1	13.0	1.1
	20	81.0	87.0	158.6	19.0	44.4	13.0	0
	30	82.0	87.0	158.1	18.0	41.7	13.0	2.9
	40	86.0	88.0	157.6	14.0	18.8	12.0	3.5
—40	2.5	20.0	26.0	173.6	80.0	116.9	74.0	112.2
	5	26.0	36.0	174.5	74.0	112.9	64.0	102.8
	10	53.0	59.0	171.5	47.0	87.0	41.0	74.4
	20	79.0	81.0	160.6	21.0	35.5	19.0	20.2
—45	10	46.0	51.0	177.7	54.0	101.6	49.0	93.3
	20	61.0	65.0	172.3	39.0	79.8	35.0	68.8
	30	82.0	84.0	162.5	18.0	28.9	16.0	9.5
	40	81.0	83.0	161.6	19.0	36.0	17.0	17.8
—47.5	10	41.0	45.0	179.5	59.0	105.8	55.0	73.2
	20	55.0	60.0	173.9	45.0	90.3	40.0	24.2
	30	68.0	71.0	170.6	32.0	66.0	29.0	11.6
	40	72.0	76.0	166.2	28.0	......	24.0	......
—60	10	16.0	22.0	185.3	84.0	128.8	78.0	124.6
	20	29.0	35.0	183.2	71.0	117.9	65.0	111.9
	30	39.0	43.0	181.9	61.0	108.4	57.0	103.3
	40	50.0	55.0	180.0	50.0	95.1	45.0	86.1
—76	10	5.0	8.0	195.1	95.0	134.1	92.0	132.1
	20	11.0	15.0	192.9	89.0	131.6	85.0	128.8
	30	13.0	16.0	190.1	87.0	129.3	84.0	127.2
	40	16.0	18.0	189.0	84.0	127.6	82.0	126.1

afforded material with an iodine number as low as 84.7 (61.3 if corrected for holdup) in rather small yield.

8. Crystallization of the mixed acids of soybean oil showed much better separation than did crystallization of the oil.

9. By a single crystallization of mixed acids, a yield as high as 50 percent of acids with an iodine number of 180 was obtained.

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Report of the Referee Board
1942-1943

Twenty-six referee chemists were appointed for the year 1942-43.

Ten check samples of cottonseed, five of crude soybean oil, four of crude cottonseed oil, and one of crude peanut oil were distributed to Referee Chemists and a still larger number of voluntary collaborators.

The retiring Referee Board has no recommendations to make to the Society or to the incoming Board, but a few comments on the year's experience may be in order.

The one peanut oil sample was selected so as to be representative of a type of oil on which erratic refining losses had given considerable trouble in commercial grading. The refining losses reported by the collaborators showed somewhat more irregularity than on the average sample of cottonseed oil, but were not sufficiently discordant to prove that the refining method is defective.

While only minor difficulties were encountered in carrying out the year's program on check samples, the effect of war conditions was noticeable. There were more delays than usual in mail and express service. Special conditions made it difficult for some of the collaborators to find time to examine the samples. Twice we were dangerously near to a critical shortage of satisfactory containers for the samples. There is no indication that war conditions will make it impossible to carry out a full program of collaborative tests during the coming season, but possibly the Society in its Annual Meeting, or the Governing Committee, or the incoming Referee Board may wish to consider whether or not such a program is appropriate for the coming year.

For handling of the tabulation of the check seed and check oil samples, the Referee Board and the Society are deeply indebted to Messrs. Doughtie, Dollear and Wheeler.

G. W. Agee
J. P. Harris
Lamar Kishlar
H. S. Mitchell
A. S. Richardson, *Chairman.*