The Separation of Solid Fatty Acids from Liquid Fatty Acids by the Formation of Acid Soaps. I. Tallow Soaps

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Abstract

The formation of acid soaps has been used successfully for the separation of a mixture of fatty acids into high and low iodine value fractions. The acid soaps of saturated acid can be made to crystallize from water leaving their unsaturated counter parts in solution. Acid soaps of saturated fatty acids are well characterized compounds with the formula R-COOM.R-COOH, where R is a straight alkyl chain, and M is sodium, potassium or ammonium.

Optimum crystallization conditions involve a soap concentration of 2–5%, pH adjustment to between 7.0 and 8.0, an initial crystallization temperature not below 25C, and a crystallization period of at least 4 hr during which time cooling to a final temperature of 5–10C must be gradual, and agitation gentle.

INEDIBLE TALLOWS and greases are by-products of the meat packing industry and their economic history is so varied that they have at times been worth no more than the net cost of their contained glycerol, plus the fuel value of their fatty acids. In addition, the long established pressing process for separating fats into the more valuable stearine and oleine is demanding on raw material quality and extravagant on manpower. The soap market, moreover, was very competitive even before the arrival of synthetic detergents, so neither outlet offered much satisfaction to the inedible fat producer. This was the background that forced meat packers into the chemical industry. When the work reported here was started in 1953, it seemed that the field of fatty acid separation was already well filled by the Emersol (1,2) and Texaco-Armour (3,4) crystallization processes, and the then new Trendex (5) solvent leaching process.

Some observations by Tomlinson (6) offered a chance of a novel process, despite the generally accepted unsatisfactory nature of soap crystallizations. Working some 20 years ago on the loss of detergency of laundry soaps in softened water, he found that carbon dioxide could inhibit foaming of tallow soap solutions without forming any immediate precipitate, though a gradual deposition of the acid soaps of the saturated acids occurred, leaving in solution the acid soaps of the unsaturated acids. He found that the reaction

$$2\ \text{Na soap} + H_2CO_3 = \text{NaH disoap} + NaHCO_3$$

could be demonstrated almost stoichiometrically by a foam titration end-point, but that as a method of fatty acid separation it was only operative in dilute solutions of about 1% soap concentrations.

The acid soaps of saturated acids are well characterized compounds with the formula R-COOM.R-COOH, where R is a straight alkyl chain, and M is sodium, potassium, or ammonium (7). Their crystal structure, as shown by long spacings in X-ray diagrams, contains two fatty acid chains with their polar ends adjacent, presumably with the hydrogen and alkali atoms not assigned specifically to either chain. They are less soluble in polar solvents than the neutral soaps, but in the absence of such solvents seem to be metastable with respect to neutral soap plus fatty acid, since they melt incongruently and are frequently decomposed by nonpolar solvents (8). Technically, they have received no evaluation (except for sodium hydrogen diacetate, commercially available as a baking aid) beyond suffering occasional blame for the high viscosity troubles found during soap stock acidulation.

Experimental

Preliminary trials confirmed the Tomlinson results; but it appeared that the concentrations used could be raised substantially by carbonating warm and then cooling, though the conditions of cooling were critical. The difficulties in separating the precipitate from the solution were also great. At this stage in the investigation, moreover, the use of organic acids or inorganic acids stronger than carbonic failed to give useful degrees of separation. This was later found to have been misleading; it was also found that tallow

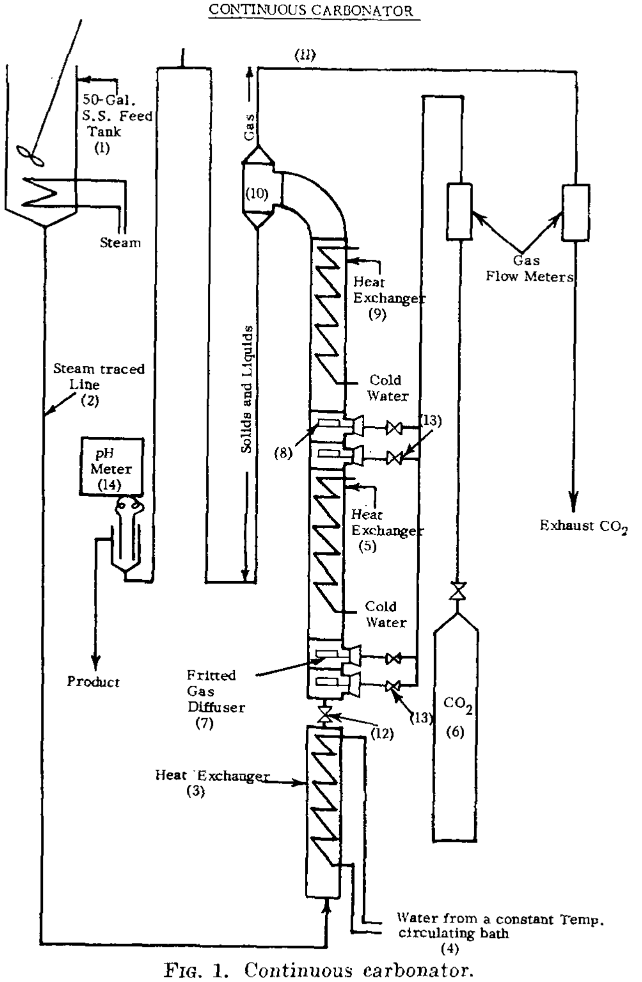

FIG. 1. *Continuous carbonator.*

fatty acids were by far the most difficult to separate. However, by this time the bulk of the work on the effect of process variables had been carried through on a tallow basis.

It was apparent that reproducible results could only be obtained with the close control of the process variables, and that the initial heterogeneous stage of carbonation was especially difficult to control on a batch scale. Continuous carbonation was found to give much more consistent results, with the obvious added advantage of not being limited in output. The viscosity of soap solutions increases steeply on cooling, though this is much less marked after carbonation. Hence, carbonation had to be started warm but could then be completed at a lower temperature. The carbonating apparatus consisted of a vertical column of 3 glass coil heat exchangers, each of 2 ft^2 cooling area, with 2 pairs of fritted disc gas diffusers between them, introduced via 1½ inch diam glass pipe tees. The input and exhaust of the carbon dioxide was metered, and the carbonated liquid was monitored as to pH and temperature (Fig. 1).

A typical laboratory carbonation was: a 2.5 to 5% solution of the sodium soap of tallow fatty acids was prepared in the feed tank 1) by dissolving the required amount of soap in water. The water was heated and agitated to facilitate solution. This solution was then fed through a stream-traced line 2) to the bottom of the carbonation tower. As the soap solution passed up through the first heat exchanger 3) it was adjusted to a constant temperature (i.e. 50C) suitable for carbonation. From the heat exchanger the soap solution passed upward through the tower. Carbon dioxide was introduced at this point through fritted glass diffusers 7). Following the initial acidification, it was possible to reduce the temperature of the soap solution and this was done in a second heat exchanger 5) where the temperature was reduced to around 35C. Further carbon dioxide was introduced at this point 8). The soap solution proceeded up the tower through a third heat exchanger 9) whereby the temperature was further reduced to about 25C.

Excess CO_2 was separated from the acidification solution by a separator 10), and was passed overhead 11) to exhaust. The rate of flow of the soapstock through the tower and the quantity of carbon dioxide admitted were controlled by valves 12) and 13) respectively, to provide a pH of about 7.2 as the solution left the carbonation tower. This pH was determined by the pH meter 14).

The acidified solution at 25C was put in 12 l flasks and held under quiescent conditions for a crystallization period of 3 to 6 hr, usually placed in a refrigerated room (zero C) so that the solution cooled to below 10C.

The crystallized mass was then filtered using a precoated leaf filter. The clear filtrate contained the acid soaps of the unsaturated fatty acids. The precipitate, which was removed from time to time with some of the filter aid, contained the acid soaps of the saturated fatty acids. Both fractions were further acidified with either HCl or H_2SO_4, heated, and the molten acids separated from the aqueous phase.

Using this equipment, a number of variables affecting the separation were studied.

The Effect of Carbonation Conditions

In order to keep 2% tallow soap solutions above the gel point, the carbonation was started at 55C. Cooling could then be applied safely, without gel formation on the heat transfer surfaces, after which carbonation could be completed at lower temperatures, with better gas absorption efficiency and control. Samples of about 12 l of carbonated stock were taken under steady operating conditions, and allowed to stand overnight at 25C, when clear supernatant liquor was acidulated and the fatty acids isolated.

TABLE I

The Effect of Carbonation Conditions

1.8% Sodium tallow (original IV 42.4) soap solution, carbonated at an initial 55 ± 1C., controlled to ± 0.1 pH

pH of solution before crystallization	Temp. of solution before crystallization ± 1C	Degree of settling first 24 hr	% Clear solution decantable after first 24 hr	IV of liquid fatty acids
7.5	35	poor	....	....
7.2	35	poor	....	....
6.9	35	poor	....	....
7.5	30	poor	....	....
7.2	30	good	63	65.4
6.9	30	good	75	66.1
7.5	25	good	61	65.7
7.2	25	good	63	67.4
6.9	25	poor	....	....
7.5	20	poor	....	....
7.2	20	poor	....	....
6.9	20	poor	....	....
7.5	14	none	....	....
7.2	14	none	....	....
6.9	14	none	....	....

These results indicate that the degree of cooling during or immediately after carbonation is important for the production of a crystalline, well settling, precipitate. The pH seems to be less critical, a range of from 7.0 to 7.5 giving operable conditions at 25–30C exit temperature.

The Effect of Crystallization Temperature

It was found that the lower the temperature, the better the degree of separation on the unsaturated side. Thus, lower temperatures gave steadily rising iodine values and falling yields of the soluble oleic fraction, but only slightly higher IV for the increasing yield of the saturated insoluble phase. It was difficult to isolate this temperature effect from other variables, as in many runs only the unsaturated acid fraction could be properly isolated; but the overall picture was clear. Typical though selected results are oleic acid fractions of IV 66 at 25C., 81 at 15C, and 85 at 12C from tallow (IV 42.4) and of IV 86 at 25C, 96 at 15C, and 101 at 5C from IV 56.9 tallow.

The Effects of Speed of Cooling and Time of Crystallization

In replicated experiments with the same conditions of carbonation, time of crystallization, and ambient temperature during crystallization, great variations in the speed of settling were still observed. These variations could be correlated with the scale of operation, and also with local air circulation conditions, both pointing to a need for maximum slowness and steadiness of cooling. Initial rapid cooling to 30C during or immediately after carbonation was found to be permissible, but the maximum rate of cooling thereafter should not exceed 10C per hr, and no warming up should occur. Vigorous agitation, over-rapid cooling, or any marked warming up, all cause the precipitate to become so finely divided that it will neither settle nor filter properly.

Slow cooling automatically involves a prolonged crystallization time, but with maximum acceptable rates of cooling there was still a definite further minimum crystallization time required. Figure 2 illustrates this. Runs were carried out under similar conditions, 2.0% soap solution being carbonated at

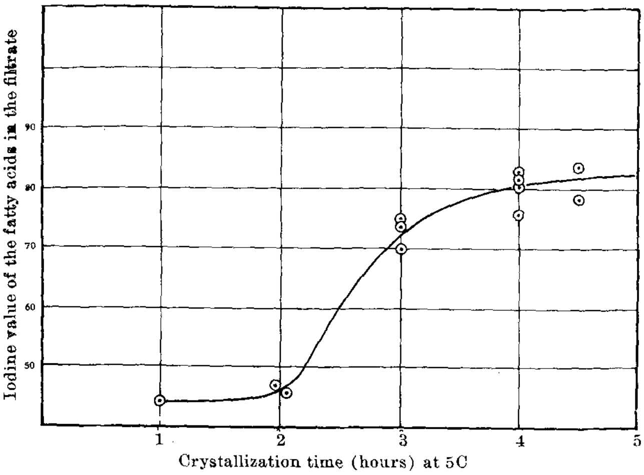

FIG. 2. The effect of crystallization time on the enrichment of unsaturated fatty acids in the mother liquor.

an initial temperature of 50 ± 1C, and a final temperature of 30 ± 1C and final pH of 7.3 ± 0.3, the products being placed in 12 l flasks in a storage room at 5C. The progress of the crystallization was followed by analyzing the filtrate obtained, using a precoated test leaf (0.1 ft^2) filter.

It is difficult to separate speed of cooling from the length of time for crystallization, but a minimum total time of 5 hr in addition to a cooling rate not exceeding 10C per hr seems essential. Later work with a continuous precoat filter confirmed this, shorter crystallization times leading to poor results in both rates of filtration and quality of filtrate.

The Effect of Soap Concentration

Since all concentrations used were above the critical micelle concentration, variations in the strength of the soap solution would be expected to affect the operating difficulties, but not the inherent degree of separation. This was confirmed (Table II) in a series carbonated at 50C, with cooling to 30C at pH about 7, and holding at 25C. Where the carbonated liquor was thin enough to handle (in a Sharples Super Centrifuge at 20,000 *g*) the IV of the filtrate fraction showed little variation, but that of the saturated fraction rose with the increasing difficulty of removal of the mother liquor.

These results indicate an operating range of up to 10% tallow soap concentration; but later work on filtration showed a strong preference for the more dilute range of 2.5 to 5% solutions.

Crystallization Promoters

Neutral fat is reported (9,10) as aiding the crystallization of fatty acids from methanol, and so a search was made for promoters to aid acid soap crystallization. One and 2% of tallow were added to the soap solution, or 1% of dispersed stearic acid, aluminium stearate, gelatine, sodium chloride, glycerol, or the commercial flocculating agents Lytron 886, 887, and 889 were injected immediately prior to carbonation. The effect was judged by the speed of settling of the insoluble acid soaps, and no advantage was found for any agent; some were strongly deleterious. The effect of seeding by the addition of 10% by volume of a previously well crystallized carbonation batch was also ineffective.

TABLE II

The Effect of Concentration of a Tallow (IV 42.4) on the Separation of Acid Soaps

Concentration of soap solution (as % FFA)	IV of solid fatty acids	IV of liquid fatty acids
13	.... too thick	to separate ....
11	.... too thick	to separate ....
10	15.8	65.6
5	13.0	65.8
2.5	9.2	68.0

The Separation of the Phases

Direct filtration of the crystallized carbonated soap stock was entirely ineffective throughout the work, even when the cooling and crystallization stage was lengthened to several days by cooling in large Dewar flasks. Either the phases passed through unseparated, or the filter blocked immediately with a thin slimy cake. Well crystallized batches, for which good settling properties were regarded as the best criterion, would filter well with a filter aid on a precoated filter, but only under exceptionally favorable conditions could the filter aid be omitted. Even then only thin cakes could be built up on the pre-coat before filtration ceased.

Good gravity settling of the precipitated acid soaps could be obtained consistently on low (2–3%) concentration soap solutions with clear supernatant volumes running around 75–80%. This offered an easy means of obtaining fair yields of the soluble oleine fraction, but left unsolved the problems of the handling of the solids, as even at 80% settling of a 2% acid soap solution, the thickened portion contained only 5% solids. The settled solids were still not amenable to filtration, but could be concentrated up to 20% by centrifugation; the residual mother liquor contamination was then removed by resuspending in distilled water, and centrifuging again. Table III.

These results show a considerable improvement on the oleine side, due to the advances in crystallization technique employed, but they point out a fundamental limitation on the stearine side, since the IV of 8 after double washing must represent unsaturation which is crystallized and not merely entrained in the solids. This is probably partly due to the *trans* octadecenoic acids naturally present in ruminant fats, but partly also to genuine co-crystallization of *cis*-oleic acid. Thus the degree of separation possible in a single stage acid soap process is that available from a lead salt separation rather than that of a solvent crystallization of the free acids.

During experiments on the resuspending and washing of the settled solids, water saturated with CO_2 was used at times as a partial buffer against soap hydrolysis; it was observed that shaking with air under these conditions led to a high degree of flotation of the solids. Analysis showed that this was

TABLE III

The Fractionation of Tallow Fatty Acids Obtained Utilizing Settlement for the Physical Separation of Acid Soaps
(Tallow Soap Stock—IV 43.6)

Items	Tests							
	1	2	3	4	5	6	7	8
% Tallow fatty acids in the soap stock	2.0	1.8	1.8	1.9	1.9	1.7	1.7	1.7
Settling temperature (°C)	25	25	25	10	10	25	25	25
Settling time (days)	¾	¾	2	¾	¾	3	6	6
% Decantable as clear supernatant	75	79	75	46	55	71	75	84
IV of liquid acids	71.0	70.4	75.6	80.6	77.5	73.4	76.9	76.0
IV of solid acids	........Centrifuged........					Not centrifuged		
	13.0	11.9	14.3	12.9	14.6	25.0	23.6	22.1
IV of the solid acids after one washing with distilled water	9.0	8.7	9.0					
IV of the solid acids after the second washing with distilled water	....	8.1	8.0					

TABLE IV

The Fractionation of Tallow Fatty Acids Obtained Utilizing Flotation for the Physical Separation of Acid Soaps

Strength of soap soln. treated	IV of tallow	IV of solid acids	IV of liquid acids
1%	42.8	15.0	65.9
2%	42.8	14.2	79.1
2%	56.5	5.9	69.0
2%	56.5	9.8	79.9

TABLE V

The Fractionation of Tallow Fatty Acids Obtained Utilizing Centrifugation for the Physical Separation of the Acid Soaps

Strength of soap soln.	Centrifuge tested	No. of *g*'s developed	Residence time	IV of solid acids	IV of liquid acids
ca. 2%	International cup-type centrifuge	ca. 1,000	1 hr	28.2	79.1
ca. 2%	International cup-type centrifuge	ca. 1,000	1 hr	15.9	78.5
ca. 2%	Sharples super centrifuge	ca. 20,000	very slow	10.0	63.6
5.2%	Sharples super centrifuge	6–7,000	1 min	......	66.3
2.4%	Sharples super centrifuge	6–7,000	2 min	......	65.5
2.4%	Sharples super centrifuge	6–7,000	1 min	......	67.4
2.4%	Sharples super centrifuge	6–7,000	2.5 min	......	62.2

mostly genuine flotation of the acid soaps, and not due to an acidulation to the lighter fatty acids, though surface conversion to free fatty acids was probably an important factor in aiding flotation.

It can be seen from table IV that promising results were obtained by flotation; but it was found difficult to float the larger particles which were characteristic of the experiments where better settling occurred.

A slurry which settles well under gravity would be expected to respond well to centrifugation. A typical well crystallized batch from tallow of IV 42.4 was centrifuged under varying conditions (Table V) but the results were generally disappointing, especially those at the highest centrifugal force.

The super-centrifuge failed at all times to give a clear effluent, even at the maximum rpm. Lowering the feed-rate caused the results to be even more disappointing, an effect which is unexplained. Working up the acids from the two phases was simple; the fatty acids were recovered by acidification, warming being necessary for a good phase separation.

Summary

Beef tallow acids of IV 45 yield about 45% of red oil of IV 80–85, and 55% of crude stearic acid of IV 10–20. Tallow acids of IV 60 give equal weight yields of fractions having IV 95 and 25.

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The Separation of Solid Fatty Acids from Liquid Fatty Acids by the Formation of Acid Soaps. II. Pilot Plant Studies

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Abstract

On contemplating pilot plant scale-up of the acid soap process for separating fatty acid mixtures into low and high iodine value fractions, improvements were desirable in acidifying agent used, and the method of separating the solid acid soaps. A further objective was to determine the range of applicability of the process.

Studies indicated that CO_2 can be replaced by mineral acids, or by the fatty acids themselves. A continuous precoat vacuum filter is suitable for the separation of the solid acid soaps. The process is applicable to refinery foots as well as to distilled and undistilled fatty acids.

PART I OF THIS SERIES (1) reported that tallow fatty acids could be separated into high and low iodine value fractions by the crystallization of their acid soaps from water. As in conventional crystallization processes, the more saturated acids concentrate in the crystalline fraction.

It was found that crystallization conditions were critical, optimum conditions involved a soap concentration of 2–5%, pH adjustment between 7.0 and 8.0, initial crystallization temperature not below 25C, and a crystallization period of at least 4 hr, during which time the cooling to a final temperature of 5–15C must be gradual, and agitation gentle.

On contemplating the scaling-up of this process, three areas of development appeared necessary:

1) A more convenient acidifying agent was required, preferably an inorganic acid.
2) A better means of separating the acid soaps.
3) The application of the process to a wider range of fatty acids, including stocks in other forms such as vegetable oil refining foots.

Experimental

Fractionations Using Mineral and Fatty Acids Instead of Carbon Dioxide as Acidifying Agents. In the work reported in Part I, carbon dioxide was used as the source of acidity. The reactions were closely controlled by means of pH, aided by the buffering action of the bicarbonate formed. Since the solution from which acid soaps are crystallized represents an equilibrium between fatty acids and their normal soaps, it should be possible to approach the equilibrium from either side—that is, one should be able to add:

1) half an equivalent of alkali to one equivalent of fatty acid, or
2) half an equivalent of mineral acid to one equivalent of soap, or
3) one equivalent of fatty acids to one equivalent of soap.

The method of reaching the required equilibrium is identified as the "neutralization history" of the solution. Some typical results are contained in Table I.