Determination of Yields in Processing Low Grade Fats

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MATERIAL control of fats and their hydrolysis products presents many difficulties. When the fats consist of the lower grades of inedible greases and tallows such as are usually used in the production of animal fatty acids, the problem becomes one that requires the most careful physical measurements and chemical analyses. Inedible fats are partially hydrolyzed as purchased and undergo further hydrolysis in storage. Some of the glycerine thus formed remains dissolved or suspended in the fat and is lost when the fat is acid washed prior to splitting. Further glycerine losses are experienced during filtration and evaporation of sweetwaters. Stubborn emulsions sometimes form during the early stages of processing, and while a considerable amount of fat can be recovered by proper handling of the emulsions, some is lost. Fatty acid losses occur during distillation and in subsequent operations such as bleaching.

A strict accounting of all losses, however small percentage-wise, is necessary because of the relatively high cost of the fats and the large volumes involved. Before endeavoring to determine the nature and extent of the losses, it is of course necessary to know the amounts of fatty acid and glycerine available from the various inedible grades of tallows and greases processed. It was found that theoretical yields, calculated from the ester value of high grade fats on the assumption that all the neutral fat is present as triglycerides, agreed well with actual yields. The theoretical fatty acid yields for low grade fats, however, are considerably higher than those obtained by gravimetric analysis while the theoretical glycerine yields are appreciably lower than those obtained by direct analysis. Data showing the variation between theoretical and actual yields on representative low grade fats are discussed in the first part of this paper.

Part I. Methods Used for Determining Yields from Low Grade Fats

THE tests now used for the grading, purchase, and sale of fats include moisture, soluble and insoluble impurities, unsaponifiable, free fatty acid, and total fatty acid. The latter two tests are determined volumetrically and are usually expressed as percentage of oleic acid. The free fatty acid (FFA) and total fatty acid (TFA) tests mentioned in this discussion were computed, using the mean molecular weight found for the fatty acids separated from the fat in question. Glycerine yields, however, were computed using 276 as the mean molecular weight of the fatty acids and 866 as the mean molecular weight of the triglycerides in the animal fats considered here. The figure 276 represents the mean molecular weight of the fatty acids separated from a large number of inedible animal fats, and 866 represents the mean molecular weight of the triglyceride of those fatty acids. Using these figures, complete hydrolysis of such triglycerides should yield 10.6% of glycerine and 95.6% of fatty acids, or a total yield of 106.2%, the percentages being based on the weight of triglycerides present. Assuming all the neutral fat to be present as triglycerides, the theoretical glycerine yield may be computed as follows:

$$\text{Theoretical glycerine yield in percentage} = \frac{0.106 \times 866\,(\%\ \text{TFA} - \%\ \text{FFA})}{3 \times 276}$$

Simplifying, the above expression becomes:

$$\text{Theoretical glycerine yield in percentage} = 0.111\,(\%\ \text{TFA} - \%\ \text{FFA})$$

Upon hydrolyzing a fat, its unsaponifiable matter remains in the fatty acid and is considered a part of the fatty acid yield in the work reported here. On the assumption that the ester value is due to triglycerides, the theoretical fatty acid yield may be computed as follows:

$$\text{Theoretical fatty acid yield in per cent} = \%\ \text{TFA} + \%\ \text{unsaponifiable}$$

To check on the reliability of the above formulae for determining theoretical glycerine and fatty acid yields it was necessary to compare yields thus computed with those actually obtained by direct methods. Samples were accordingly drawn from each of six storage tanks containing raw fat varying in quality from extracted grease to a mixture of prime and special tallows. The storage period of the stock in these tanks varied from 1 week to 14 months, and the contents of one tank were in an advanced stage of hydrolysis due to a leaking steam coil.

Moisture, soluble and insoluble impurities, unsaponifiable, free fatty acid, and total fatty acid were determined on each sample by the A.O.C.S. Methods (1), and the theoretical glycerine and fatty acid yields calculated using the above formulae.

The A.O.C.S. Dry Extraction Method for Total Fatty Acids of Soap Stock and Acidulated Soap Stock (1) was used for the gravimetric fatty acid determination. Unsaponifiable matter is included with the fatty acids by this method. Fatty acids separated from inedible fats contain an appreciable amount of material which resembles oxidized fatty acids as it is insoluble in petroleum ether but soluble in ethyl alcohol. This material is not removed in acid washing or splitting but is almost entirely removed by distillation, being concentrated in the residue and eventually leaving the process with the stearine pitch. For this reason it should be included in the yield, and the Dry Extraction Method was therefore modified to the extent that the petroleum ether extraction was followed by an alcohol extraction, and the sum of the extracts considered as the fatty acid yield.

The aqueous glycerine solution separated during the course of the Dry Extraction Method was analyzed by the A.O.C.S. Method for Glycerol in Commercial Soaps and Soap Products (1). This method is based on oxidation with potassium dichromate and

the percentage of glycerine obtained includes any oxidizable impurities not removed by the silver sulfate purification. As a check on the accuracy of this method 500-gram samples of fresh and stored fats were Twitchellized using three boils, the combined sweetwaters neutralized with lime, filtered, and concentrated to semi-crude glycerine under vacuum. The glycerol content of the semi-crude was then determined by the acetin method. The glycerine remaining in the split fatty acids was determined by saponifying 10 grams of the split fatty acids and then applying the A.O.C.S. Method for Glycerol in Commercial Soaps and Soap Products (1). Approximately 0.4% glycerine was found in the Twitchellized fats. The glycerine found in the semi-crude by the acetin method plus the small amount remaining in the split stock consistently averaged about 0.4% less than the amount obtained by the dichromate method. For example, a composite representing a half million pounds of fresh Special and Prime Tallow contained 9.52% glycerine as determined by the dichromate method, but only 9.12% was obtained by the check method. Another composite sample representing several million pounds of stored and acid-washed Diamond S. Tallow and Yellow Grease Stearine analyzed 7.98% by the dichromate method, but only 7.59% could be accounted for by the check method.

The acetin method has been confirmed by the A.O.C.S. and other investigating committees as giving results nearer to the truth than the dichromate method on crude glycerine. The dichromate method has, of course, the great advantage of rapidity over the acetin determination and, unlike the latter method, can be applied to very dilute glycerine solutions. For routine determinations of glycerine yields it is therefore much preferred over the acetin method. In view of the tests obtained by the check method it was considered advisable to correct the dichromate results on the six samples of fat analyzed by making a subtraction of 0.40%. The corrected result is referred to in Tables I and II as the Actual Glycerine Yield.

In Table I are shown the analytical data and theoretical and actual yields of glycerine and fatty acid on the six samples of fat analyzed by the methods described above. A better comparison of the theoretical and actual yields is obtained if the results are computed to a moisture- and impurity-free basis as shown in Table II.

It will be noted from Table I that every sample yielded considerably more glycerine than was calculated from its ester value. With the thought that the presence of free glycerine might explain the differences Samples B and D were water washed before determining their glycerol content. These results are given in Table III along with previously determined glycerol contents before water washing and those calculated from the ester value.

TABLE III

	Sample B	Sample D
Glycerol content before water washing	6.2%	8.2%
Glycerol content after water washing	6.0%	8.1%
Glycerol content as calculated from ester value	4.1%	7.1%

The tests shown in Table III indicate that free glycerine accounts for only a small part of the difference between the actual and theoretical results. Animal fat triglycerides average about 10.6% glycerine whereas the di- and mono-glycerides average about 15.1% and 26.3%, respectively. The fact that the actual glycerine yield exceeds the theoretical yield might therefore be accounted for by the presence of mono-glycerides or, more probably, by the presence of di-glycerides. An indication that this is the case was found when acetyl values of 30 to 45 were obtained on several samples of acid-washed low grade animal fats. The acetyl values, determined by the A.O.C.S. Method (1), may have been high because of possible interference by the substantial quantity (34% to 37%) of fatty acids present in the fats (2). Oxidized fatty acids present in low grade fats would also be responsible for part of the acetyl value of such stocks (3). It is planned to continue this phase of the investigation by determining the acetyl values of low grade animal fats by the pyridine-acetyl chloride method of Smith and Bryant (4) and by the mixed methyl ester method described by Grün (5).

As further evidence of the unreliability of calculating glycerine yields of low grade fats on the basis that

TABLE I (AS IS BASIS)

Sample	A	B	C	D	E	F
Description of Fat	Dia. A. Tallow Yel. Gr. St. Sp. Tallow	Dia. S. Tallow No. 1 Tallow Sp. Tallow	Extracted Grease	Dia. S. Tallow No. 1 Tallow Sp. Tallow	Pr. Tallow Sp. Tallow	Dia. S. Tallow No. 1 Tallow Sp. Tallow
Storage Period in Months	2	14	6	5	10	¼
Moisture	0.32	2.52	1.25	0.66	0.41	0.48
Soluble and Insoluble Impurities	0.04	0.47	0.06	0.11	0.02	0.51
Unsaponifiable Matter	0.74	0.86	3.28	0.63	0.61	0.67
Gravimetric Fatty Acids (Pet. Ether Soluble)	94.63	93.23	91.89	94.46	94.23	93.92
Oxidized Fatty Acids (Ethyl Alcohol Soluble)	0.49	0.21	1.63	0.21	0.30	0.32
Glycerine (By Dichromate Method)	9.21	6.57	7.87	8.61	9.74	9.52
Free Fatty Acid (Calc. to Mol. Wt. Found)	22.8	58.2	36.3	31.3	27.1	14.8
Total Fatty Acid (Calc. to Mol. Wt. Found)	95.6	95.1	92.3	95.8	95.7	94.6
Molecular Weight of Separated Fatty Acids	276	277	276	275	277	276
Theoretical Glycerine Yield in Percent	8.1	4.1	6.2	7.1	7.6	8.85
Theoretical Fatty Acid Yield in Percent	96.3	96.0	95.6	96.4	96.3	95.3
Theoretical Total Yield in Percent	104.4	100.1	101.8	103.5	103.9	104.15
Actual Glycerine Yield in Percent	8.8	6.2	7.4	8.2	9.3	9.1
Actual Fatty Acid Yield in Percent	95.1	93.4	93.5	94.6	94.5	94.7
Actual Total Yield in Percent	103.9	99.6	100.9	102.6	103.8	103.8

TABLE II (MOISTURE AND IMPURITY FREE BASIS)

Theoretical Glycerine Yield in Percent	8.1	4.2	6.3	7.2	7.6	8.9
Theoretical Fatty Acid Yield in Percent	96.7	99.0	96.9	97.1	96.7	96.2
Theoretical Total Yield in Percent	104.8	103.2	103.2	104.3	104.3	105.1
Actual Glycerine Yield in Percent	8.8	6.4	7.5	8.3	9.3	9.2
Actual Fatty Acid Yield in Percent	95.5	96.3	94.7	95.3	94.9	95.6
Actual Total Yield in Percent	104.3	102.7	102.2	103.6	104.2	104.8

all the neutral fat is present as triglyceride, there was one six-month period when production plus known losses of glycerine averaged 7.1% of the fat split whereas the theoretical yield as calculated from the neutral fat content was only 6.5%.

It will be noted from Table I that the theoretical fatty acid yield exceeds the actual yield by 1.2% to 2.7%. During the course of this work it was noticed that the amount of alkali required for saponification of the raw fat was always appreciably greater than that required for the saponification of both the petroleum ether soluble fatty acids and the oxy fatty acids separated from the fat. This means that some of the saponifiable material in the raw fat is lost or modified during the process of separating the fatty acids. It is therefore likely that the mean molecular weights are too high since they were calculated from the weight and alkali requirements of the separated fatty acids. A high molecular weight would give high results for the free and total fatty acids and explain the discrepancy noted.

In summary, then, this investigation of low grade animal fats indicates the advisability for determining fatty acid yields by a gravimetric method and for determining glycerine yields by actual analysis. The A.O.C.S. Dry Extraction Method for Total Fatty Acids of Soap Stock and Acidulated Soap Stock (1) is recommended for determining the fatty acid yield gravimetrically provided the method is modified to include the petroleum ether insoluble but alcohol soluble fatty acids. The A.O.C.S. Method for Glycerol in Commercial Soaps and Soap Products (1) gives uniformly high results when applied to low grade raw fats. For all practical purposes glycerol yields obtained by this method on such fats should be corrected downward by 0.4%.

Inventories of raw fat and partially split fats in a fatty acid plant should be kept on the basis of available glycerine and fatty acids so as to obtain a true picture of actual yields and processing losses. The methods herein discussed for determining actual yields parallel fatty acid plant operations and for this reason should give accurate information on the maximum yields attainable.

Part II. Discussion of Processing Losses in a Fatty Acid Plant

THE principal causes of glycerine loss were found to be as follows:

1. Hydrolysis in storage.
2. Acid washing.
3. Non-recovery of glycerine retained in calcium sulfate cake obtained from sweetwater filter presses.
4. Carry-over in glycerine evaporators.
5. Non-recovery of glycerine from sediment periodically removed from glycerine evaporators.
6. Incomplete hydrolysis of fats.

Loss due to hydrolysis in storage and acid washing may easily amount to as much as 11% of the glycerine available from the fat as received, particularly if the fat has been in storage for many months. Some of the glycerine liberated during storage is found in the water drained from storage tanks and is not usually recovered because of the impurities it contains. A considerable amount of the glycerine liberated by hydrolysis in storage and acid washing is found in the waste water drained from the acid washing tanks. The waste water contains so much sulfuric acid and impurity removed from the fat that recovery of saleable glycerine is difficult and hardly economical. The best solution for limiting glycerine losses due to these causes is to acid wash and split the fats as soon as possible, preferably immediately upon receipt.

The calcium sulfate removed from the sweetwater filter presses contains about 4.4% glycerine, two-thirds of which can be recovered by water washing the cake before removing it from the press. The glycerol content of the wash water is but 0.7% to 1.0%, and it is not economical to process such dilute sweetwater. It should, therefore, be used as splitting water because the small amount of glycerine thus added to that obtained from the fat does not retard the rate or degree of splitting and can thereby be recovered economically. About 3% of the glycerine available from the fats as received by the splitting department is lost in unwashed cake, and this amount can be reduced to 1% by water washing.

Carry-over loss from glycerine evaporators can be serious if the liquid level gets too high or if kicking or excessive foaming occurs. Extensive input and output studies showed that with careful operation of the evaporators less than 1% of the glycerine input is entrained with the steam. Careless operation or poorly designed equipment can be the cause of much larger losses. Evaporators should be equipped with efficient separators.

The sediment which accumulates in the bottom of the evaporators should not be flushed to waste because about 2% of the glycerine available from the fats as received by the splitting department is thereby lost. The sediment, consisting for the most part of calcium sulfate dispersed in glycerine, should be flushed to the sweetwater treating tank so that the glycerine can be saved. Loss of glycerine caused by incomplete hydrolysis can be greatly reduced during the distillation operation by splitting the residues before sending them to the tar stills.

Careless processing of low grade fats will result in total glycerine losses approximating 20% or more of the glycerine available in the fats as purchased. This loss can be reduced by more than one-half by prompt splitting and careful processing methods.

The principal sources of fat and fatty acid loss are as follows:

1. Emulsions.
2. Sediment in storage and processing tanks.
3. Distillation.
4. Spent bleaching clay.
5. Poorly designed catch basins.

Proper acid washing of low grade fats is the best insurance against troublesome emulsions. Some fat, however, is emulsified with the impurities removed by acid washing. Much of this fat can be recovered by adequate settling of the emulsions, but eventually the impurities become so concentrated that settling methods fail. Most of the fat contained in such emulsions can be profitably recovered by solvent extraction. The amount of fat lost in emulsions is variable, depending upon the quality of the raw stock and operating technique.

The important loss during distillation is the result of some decomposition of the fatty acids. The decomposition products are exhausted with other non-condensable gases and represent a total loss. Another but less important loss is represented by the fatty acid carry-over into the hot well. Some of this fatty acid is

dissolved or so thoroughly emulsified in the water as to make complete recovery difficult if not impossible.

Distillation losses have been variously reported as being from a few tenths of 1% to as much as 2%. It is probable that the combined losses are somewhere between 0.5% and 1% for continuous distillation. Distillation losses can be held to a minimum by:

1. Distilling at the highest vacuum and lowest steam ratio practicable.
2. Distilling by a continuous process in corrosion resistant equipment rather than by a batch process in iron equipment, such as the old type pot stills. Decomposition is greater by batch distillation, particularly in iron stills.
3. Providing adequate condenser capacity so as to maintain carry-over at a minimum. Reduction of carry-over with the steam by installation of baffles or bubble caps in the vapor line between the condenser and barometric has long been known.
4. Splitting of residues so as to keep the neutral fat content of the feed to the tar stills as low as possible.

Spent bleaching clay resulting from the bleaching of stearic acid contains from 25% to 35% of stearic acid. On the basis of using 3% of clay to bleach the stearic acid, this represents a loss of about 1% of the stearic acid bleached or 0.4% of the raw fat. Practically all of the stearic acid can be recovered from the spent clay by solvent extraction.

The need for adequate catch basins in a fatty acid plant cannot be over-emphasized. Much of the fat and fatty acids drawn off with water and emulsions from processing tanks will separate in the catch basins and can thus be reclaimed. The sewer system leading to the catch basins should preferably carry only processing liquors so as to keep the amount of water and therefore the flow through the catch basins to a minimum. Separate pumps for each department are also desirable in order to eliminate degrading of stocks as much as possible.

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Applied Ultraviolet Spectrophotometry of Fats and Oils

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RECENT developments in spectrophotometric methods and equipment have brought about greatly increased use of ultraviolet spectrophotometry as applied to many chemical problems. Studies of fats and oils are no exception. Within the past few years a number of reference materials have been prepared and purified and used as spectrophotometric reference standards. Studies regarding the empirical isomerization of double-bond systems to bring about conjugated systems have enabled the development of quantitative spectrophotometric methods for analysis of fats and oils for their polyunsaturated constituents (1, 2, 3, 4, 5, 6, 7, 8). These methods are so simple and rapid as compared with earlier chemical procedures, and their sensitivity is so great, that there is an increasing use of spectrophotometric studies on a routine laboratory basis. The recent application of this type of method to the control of tallows and soaps is an outstanding example of such use (7, 8). Because of the rapid growth of developments in the field it is considered advisable at this time to discuss the methods of spectrophotometric analysis of fats and oils and to point out some of their applications in industry. The discussion will include sample calculations, interpretation of the absorption spectra, and other similar considerations. The studies to be discussed depend upon the fact that there are certain structures in the fat molecules known as chromophores, which absorb radiant energy in a characteristic manner. These chromophores with which we are concerned in the fatty acids are composed of double bonds. Figure 1 shows a simplified diagram of the double bond systems in several of the naturally occurring fats or fatty acids. Note that in linoleic acid and linolenic acid, as well as in arachidonic acid, the double bonds are separated from each other by two single bonds. This structure leaves the double bonds in more or less isolated systems, and they do not absorb radiant energy characteristically in the ultraviolet portion of the spectrum at wavelengths above 2100 Å. Although these systems do show characteristic absorption at shorter wavelengths, i.e. in the "vacuum ultraviolet" (9), the present discussion will be confined to the region which may be studied by an instrument such as the Beckman Model DU quartz spectrophotometer (10).

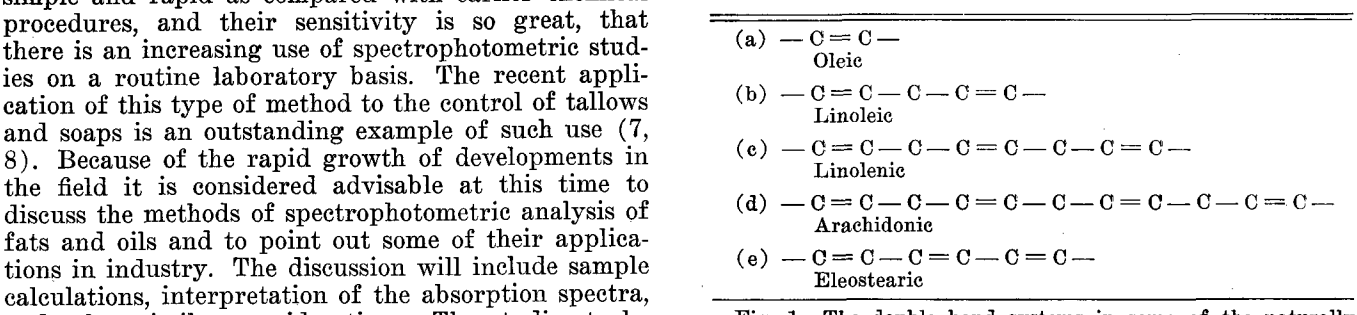

Fig. 1. The double bond systems in some of the naturally occurring fatty acids.

Because the double bonds are in these isolated positions, the ultraviolet absorption spectra of oils containing the double bond systems shown in (a), (b), (c), and (d), of Figure 1 do not possess characteristic shapes. When two or more of these double bonds are