Glycerol Distribution in Soap Boiling Operations[1]

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IN soap boiling operations it has been observed in the past (1, 2) that the glycerol retention by the water in the soap curd layer is for practical purposes the same as that in the soap lye layer. For example, if the concentration of glycerol in the water of the soap curd is 5%, then that of the glycerol in the soap lye layer is also 5%. While this relationship may exist under certain boiling conditions, it was found under others that the ratio varied.

Analytical results from several experimental boils in a 50-lb. kettle indicated that there was a marked difference between the glycerol to water ratios in the soap curd layer and soap lye layer. Under certain boiling conditions the water in the lye layer retained up to approximately one and three-tenths as much glycerol as the water in the soap curd. It was decided to test these findings on a full plant scale during normal operations. At the same time the experimental data were used to make a tabulation balancing the glycerol input and output of a soap kettle.

Experimental Details

Weights of soaps and lyes were obtained in the kettle itself with an accuracy of 2% by means of an air back-pressure liquid level gage. Samples of soap curd were taken with a zone sampler after the lye layer was withdrawn. Samples of lye, neat soap, and niger were taken as they were withdrawn from or pumped into the kettle. Glycerol was determined in the samples by the dichromate oxidation method. Water was determined by oven drying at 105°F.

Results and Observations

Several kettles were tested under varied boiling conditions for the glycerol to water percentage in soap curd relative to that in the lye layer. It was observed that when a kettle was boiled on a soft grain, the glycerol to water percentage in the curd relative to that in the lye generally approximated a one to one ratio. However, on a medium or hard grained boil, the ratio consistently ran from 1:1.2 to 1:1.3. This appears to be at variance with the conclusions of Ferguson (1) who states: "The results seem to show an approach to a ratio of about 1.0 as the electrolyte strength increases or as the soap becomes more grainy."

In general, kettles boiled on a soft fleecy grain cannot be given a vigorous boiling because they quickly puff up and fill the kettle, preventing good intermixing of the lye and the curd layer. Hard grained kettles, on the other hand, can be boiled vigorously without much swelling, bringing lye up from the bottom of the kettle to mix thoroughly into the curd layer. This difference in mixing may account in part for the lower glycerol retention of lyes on a soft grained boil compared with lyes on a hard grained boil.

In kettles boiled on a hard grain the water in the lye layer tended to hold, as an upper limit, about 1.3 times the glycerol retained by the water in the curd layer. This upper limiting ratio appears to be an equilibrium between the glycerol retention by the water in the lye and in the curd layers. It is difficult to explain why the water in the curd layer is less retentive of glycerol than the water in the lye layer. One hypothesis which appears reasonable is that the soap molecule in the curd layer contains water of hydration which is free of glycerol. This would decrease the net concentration of glycerol in the water of the curd compared with that in the lye.

TABLE I

Glycerol Distribution in a Typical Soap Kettle Boil on a Countercurrent System

	Change No. 1	Change No. 2	Change No. 3	Change No. 4
	%	%	%	%
Glycerol in curd layer	3.21	1.73	0.72	0.60
Water in curd layer	32.2	29.92	33.40	29.12
Glycerol retained by water in curd layer	10.0	5.78	2.16	2.06
Glycerol in lye	8.70	5.39	2.36	2.19
Water in lye	81.1	75.92	83.27	82.35
Glycerol retained by water in lye	10.7	7.10	2.83	2.66
Ratio of glycerol retained by water in curd layer to that in lye	$\frac{1}{0.94}$	$\frac{1}{1.23}$	$\frac{1}{1.30}$	$\frac{1}{1.29}$

Table I shows a kettle typical of those boiled with hard grained curds. The glycerol retention of the water in the lye layer runs from 0.94 to 1.30 times that of the curd layer.

TABLE II

Glycerol Balance in a Countercurrent Soap Kettle Boil

	Amount in lb.	Per cent glycerol	lb. 100% glycerol added to kettle	lb. 100% glycerol discharged from kettle
Change No. 1				
Tallow pumped to kettle	38,500	10.2	3,930	
Coconut oil pumped to kettle	16,500	13.3	2,200	
Soap lye pumped to kettle	54,300	5.46	2,960	
Spent lye discharged from kettle	57,700	8.70		5,020
Curd remaining in kettle	83,700	3.21* 1.47**		
Change No. 2				
Soap lye pumped to kettle	46,300	2.12	982	
Soap lye discharged from kettle	64,000	5.39		3,450
Curd remaining in kettle	88,600	1.73		
Change No. 3				
Soap lye discharged from kettle	45,500	2.36		1,074
Curd remaining in kettle	89,900	0.72		
Change No. 4				
Niger soap pumped to kettle	18,900	1.65	312	
Soap lye discharged from kettle	15,700	2.19		344
Curd remaining in kettle	96,600	0.60		
Change No. 5				
Neat soap discharged from kettle	81,600	0.35		286
Niger soap discharged from kettle	19,900	1.51		300
Total glycerol charged to kettle			10,384	
Total glycerol accounted for				10,474

* Free glycerol.

** Glycerol bound in unsaponified portion of fat charge.

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A glycerol balance of the same kettle used for illustration in Table I is shown in Table II. The discrepancy between the incoming and outgoing glycerol is less than 1%, which falls within the experimental error of sampling, material weighing, and chemical analyses. Somewhat less spent lye was taken off the first change than is normal, but this deficiency was compensated for in the second change when a larger than normal lye was taken off.

The percentage of glycerol left in the neat soap, 0.35%, represents a loss of nearly 5% of the glycerol actually available from the fats and oils charged to the kettle. This is equivalent to a kettle recovery of about 95%.

Conclusions

1. Glycerol distribution in the curd and lye layers approaches a ratio, as the electrolyte strength increases, in which the glycerol concentration in the water of the lye layer is about 1.3 times the glycerol concentration in the water of the curd layer. A high distribution ratio is conducive to a more effective glycerine recovery.
2. Conditions for the most favorable glycerol distribution ratio are vigorous boiling on a hard grained curd for a sufficient length of time to assure thorough mixing.
3. The yield of glycerol from the kettle was 95% exclusive of that in the neat soap.

Acknowledgment

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The Determination of Borax in Soap

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It has been found in this laboratory that the method for the determination of borax contained in a Federal Specification (1) and also in the Official Methods of the American Oil Chemists' Society (2) is both very lengthy and of unsatisfactory accuracy. The procedure involves fusing the borax-soap with sand and soda ash, solution of the fused mass in dilute acid, repeated refluxing with calcium carbonate, filtration, and titration of the filtrate with standardized alkali in the presence of mannitol or neutral glycerol to the phenolphthalein endpoint.

Blank and Troy (3) have devised a method which is claimed to be superior to the above procedure. It depends on removal of the soap by acidification and extraction of the fatty acids released, followed by quantitative precipitation of any soluble silicates, carbonates, and ortho-phosphates present with excess strontium chloride solution. Strontium metaborate is soluble under these conditions and is converted to boric acid by acidification of the filtrate, which is then titrated in the usual way in the presence of mannitol or glycerol.

Consistently low results and poor reproducibility have been obtained with the Blank and Troy method in this laboratory. It is believed that these low results are due, at least in part, to mechanical loss of borax during the removal of soap fatty acids by several extractions with petroleum ether. It was found that the soap can be quickly and completely removed by precipitation with the same precipitating reagent, strontium chloride, used to precipitate silicates, carbonates, and phosphates. In this way soap and interfering alkalies are removed simultaneously. Another refinement in the Blank and Troy method was the substitution of methyl purple indicator (4) for methyl red in adjusting the acidity of the solution prior to the final titration. Methyl purple gives a sharper endpoint than methyl red and thus is especially desirable with low borax samples. It was also found desirable to obtain complete removal of dissolved carbon dioxide from the solution before the final titration.

TABLE I

Determination of Borax in Soap-Borax Mixtures by Federal Specification Method (1)

Sample No.	Soap-Borax Ratio [1]	Borax Added (Grams)	Borax Found (Grams)	% Recovery	Average % Recovery	Average Deviation
1A	......[2]	0.0000	0.0020	......	......	......
1B	......	0.0000	0.0022	......	......	......
1C	......	0.0000	0.0024	......	......	......
2A	19:1	0.2623	0.2207	84.1	87.8	5.0
2B	19:1	0.2536	0.2416	95.3	......	......
2C	19:1	0.2545	0.2138	84.0	......	......
3A	3:1	1.2857	1.1527	89.7	90.6	1.4
3B	3:1	1.2833	1.1886	92.6	......	......
3C	3:1	1.2871	1.1506	89.4	......	......
4A	1:3	3.8479	3.6223	94.1	93.6	0.5
4B	1:3	3.8292	3.5646	93.1	......	......
5A	......[3]	5.1309	4.8306	94.2	94.5	0.2
5B	......	5.1180	4.8418	94.6	......	......
5C	......	5.1077	4.8297	94.6	......	......

[1] Total sample weight in each analysis was approximately 5 grams.
[2] Samples marked 1 are all soap and contain no borax.
[3] Samples marked 5 are all borax and contain no soap.

Analyses of soap-borax mixtures of varying ratios of soap to borax were conducted using the federal specification procedure. the Blank and Troy method, and the method described below. Soap-borax mixtures containing either trisodium phosphate or sodium metasilicate were also analyzed by these methods to determine the effect of the presence of other alkaline salts.

Materials and Reagents

The following materials were used in this study: Borax, C. P. ($Na_2B_4O_7 \cdot 10H_2O$), was assayed by a mannitol titration method given in Scott (5) and found to contain the equivalent of 102.5% $Na_2B_4O_7 \cdot 10H_2O$; this value was verified by dehydrating a