Recovery of Glycerine From Waste Products

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This laboratory, working in cooperation with the Soap and Glycerine Unit of the War Production Board (now a part of the United States Department of Agriculture), has investigated the possibility of recovering glycerine from certain waste products and by-products. The results of our work on two types of raw materials will be discussed here.

Part I—Sulfonation Liquors

(Experimental work by H. V. Clark, S. K. Coburn, E. E. Langdon and R. T. Schenck)

Thirteen samples of sulfonation liquors from six companies were accumulated, some by direct request to the manufacturers and some through the medium of the Soap and Glycerine Unit. The following analytical determinations were made on these samples: Specific gravity; acidity; ash; glycerine by periodate titration; and glycerine by actual isolation. Periodate titrations were made in the conventional manner. The results of these determinations were consistently higher than, but proportionate to, those obtained by actual glycerine isolation (see Table I).

The procedure for glycerine recovery was as follows: A sample weighing between 100 and 1000 grams, depending on the glycerine concentration as previously determined by periodate titration, was neutralized with hydrated lime under vigorous stirring. The precipitate was filtered and washed and the washings added to the filtrate. Another portion of lime amounting to about 1 to 2 per cent of the weight of the original liquor was now added to the filtrate and washings and the suspension was boiled for one hour with stirring to saponify glycerides. The suspension was filtered, the cake washed and the filtrate rendered substantially calcium-free by addition of sodium carbonate. The mixture again was filtered, the pH adjusted to about 8 with hydrochloric acid and the solution concentrated by distillation. Any salt which formed during this treatment was filtered off. The glycerine was obtained from the filtrate by vacuum distillation. Glycerine assays on several of these distillates by refractive index and specific gravity indicated 97 to 100 per cent glycerine content. Analysis of the glycerine obtained from Sample 4, Table I, by the acetin method, indicated 96.85 per cent glycerine.

Examination of Table I shows that the liquors were of such widely varying composition that the practicability of the process would have to be decided for each sample separately. In many cases rather large amounts of acid must be neutralized. Availability of vats, filters and evaporators would have to be considered.

No estimate of the total amount of glycerine recoverable from sulfonation liquors has been made because of fluctuations in the amount of oil available for sulfonation and because of the wide variation in glycerine content of the samples examined, which may or may not have been a true cross section of commercially available products.

As a possible solution to the loss of glycerine in the sulfonation of glyceride oils, a sample of methyl esters of castor oil fatty acids was prepared by ester interchange, and the glycerine recovered. The methyl esters were sulfonated, and this product was then compared with a sample of sulfonated whole castor oil prepared under the same conditions. The comparisons were made by an industrial laboratory familiar with such testing, and included tests for dye dispersion, dye leveling and retardation of dyeing, using direct colors. It was reported that there was apparently no difference in performance of the two samples.

Part II—Distillers' By-Products

(Experimental work done by H. V. Clark, E. E. Langdon, C. W. Lenth, C. S. Miner, Jr., R. T. Schenck and J. B. Segur)

It is well known that glycerine is produced in the alcoholic fermentation of carbohydrates by yeast. The concentration is so small that under ordinary conditions it is considered uneconomical to recover it. However, in view of the enormous production of fermentation ethyl alcohol as well as the demand for glycerine at the present time, it was judged advisable to investigate the feasibility of recovering glycerine from distillers' by-products.

After distillation of alcohol from a fermented grain mash, there remains a mixture of spent grains plus a dilute aqueous solution known as thin stillage. In some cases the grains are screened out, dried and sold as feed, the thin stillage being discarded. Alternatively the thin stillage may be concentrated to a syrup, remixed with the grains, and the whole further concentrated to dryness. The product makes a superior grade of feed by virtue of the additional soluble food substances contributed by the thin stillage. Almost all of the glycerine present is in the stillage. The method of recovery will depend in part on the process used in disposing of the fermentation residue.

It has been found possible to recover appreciable amounts of glycerine from both types of dried grains by extraction with butyl or amyl alcohol, with subsequent removal of glycerine from the alcoholic solution by washing with water. By this means most of the impurities accompanying the glycerine in the alcoholic extracts are left behind and the water extract contains chiefly glycerine and organic acids. Crude fusel oil is not a satisfactory source of amyl alcohol for the extraction because it contains substances which interfere with the recovery of the glycerine.

A sample of dried grains containing no added concentrated stillage gave a yield of 0.3% crude glycerine when extracted as described above. Several samples of grains plus concentrated stillage were extracted similarly and gave yields of crude glycerine varying between 1.25 and 2%. The higher figure represents a less pure glycerine which might be somewhat difficult to refine.

The acidic substances removed in the extraction comprise principally succinic and long-chain fatty acids.

TABLE I

Analyses of Sulfonation Liquors

Sample No.	Type	Sp. Gr. 27°/15.5°C. as Received	Per Cent Composition by Weight			
			Acidity as H_2SO_4	Sulfated Ash	Glycerine	
					By KIO_4 Titration	Recovered
1	High sulfonation	1.263	27.3	6.57	0.67	0.4
2	Medium sulfonation	1.199	19.2	7.28	0.12	0.1
3	Low sulfonation	1.099	10.5	0.055	8.63	6.73
4	Low sulfonation	1.125	13.3	0.037	8.72	8.30
5	High sulfonation	1.143	20.1	0.04	0.62	0.34
6	Medium sulfonation	1.155	21.9	0.04	0.44	0.33
7	Low sulfonation	1.116	16.7	0.031	0.26	0.20
8	High sulfonation	1.069	1.0	7.1	0.08	......
9	Medium sulfonation	1.142	3.7	13.4	0.25	0.19
10	Composite	1.147	2.4	13.1	4.02	3.2
11	?	1.121	2.4	20.2	0.008	0
12	?	1.121	2.4	18.4	0.005	0
13	?	1.111	0.1	10.6	1.52	1.28

Two serious disadvantages make it apparent that extraction of dried grains by the method described is an uneconomical procedure. These are: (1) The yield of glycerine is low; (2) removal of glycerine by extraction with butyl or amyl alcohol, which was found to be the preferred procedure, reduces the fat content of the grains to such an extent that their value as feed is seriously impaired. This is illustrated in Table II, which gives the analysis of distillers' dried grains containing concentrated stillage before and after solvent extraction for removal of glycerine:

TABLE II

	Before Extraction	After Extraction
	per cent dry basis	
Crude protein (N x 6.25)	32.5	36.1
Crude fat	5.7	1.3
Ash	3.8	4.0
Crude fiber	9.4	10.1

Other factors such as palatability of extracted feed, market for by-products and reuse of extractants would also have to be determined.

It was found possible to recover glycerine from dried grains by steam vacuum distillation. The yield depends upon the fineness of the grains. The highest yield obtained was 1.8% crude glycerine, when the grains were between 14 and 30 mesh. This process requires a rather large outlay of equipment.

In those cases where equipment is available to concentrate thin stillage, it is believed to be preferable to extract the glycerine from the aqueous solution in the absence of the grains. This is based on the following experimental observations.

Samples of commercial concentrated thin stillage of about 30% solids content were further concentrated by heating under vacuum and were extracted with tertiary butanol or with iso-propanol, which had previously been found to be preferred extractants. The concentrate was mixed thoroughly with about two parts of the alcohol using a high-speed stirrer, adding enough lime during the stirring to neutralize the acids present. After filtration, the alcoholic extract was distilled and a crude glycerine obtained in this way. From 60 to 80% of all material volatile at or above the boiling point of glycerine in these distillations consisted of glycerine, although the quality of that obtained in the first distillation was not high. It had a yellow-brown color and a rather pronounced, pungent, burned odor and flavor somewhat like that of glycerine obtained by the sulfite or carbonate fermentation process. A thorough study of the purification of this product was not made.

The preferred solids content of the concentrate was about 70%. The yields of crude glycerine averaged 3.1-3.9% of the 70% solids concentrate, or 4.4-5.5% on the solids basis.

Tertiary butanol appeared to be slightly better than isopropanol as an extractant because it dissolved a little less of the impurities. However, the higher price of tertiary butanol is a disadvantage.

Although it was shown that glycerine could be recovered from concentrated stillage in reasonably good yield, the process does not appear to be feasible at the present time. Availability of the following equipment would be a determining factor: evaporators for concentrating the stillage to 70% solids; stirring equipment and tanks for effecting thorough contact of concentrate and alcohol; filter presses for filtering the alcoholic suspension; and stills for removing the alcohol. On the basis of the normal operation of one grain alcohol plant, it has been estimated that to extract the concentrated stillage would require in process as much isopropyl or tertiary butyl alcohol as the stillage yields ethyl alcohol, together with the additional distillation equipment required to handle that much extra high wines. Moreover, in order to make the process economical, it would be necessary to keep the solvent losses low. The extracting alcohol would of course be recycled.

Summary

Methods of recovering glycerine from sulfonation liquors and from distillery wastes have been described. Although substantial quantities of glycerine may be recovered from these by-products, the processes are probably not economically feasible under present conditions.