LABORATORY AND PLANT

COMMENTS ON THE KREBITZ PROCESS OF SOAP-MAKING AND GLYCEROL RECOVERY¹

By G. A. WRISLEY

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The process of soapmaking by boiling fats and oils (glycerides) with caustic soda is, in general, considered the most practical process since it yields soaps of uniformly good quality, color and hardness, and at the same time a good amount of glycerol may be recovered by comparatively simple means. The yield of glycerol from the soap lye runs from 60 to 80 per cent of the total amount formed by the saponification of the fats and oils. The loss depends upon the few or many washes that the soap receives. However, it seems that no matter how careful one is to make the washes and changes on the soap, there is always some glycerol, $\frac{1}{2}$ to 1 per cent, left in the soap. It has also been demonstrated that in evaporating down waste lyes and handling so much salt which cannot be perfectly dried and freed from glycerol, that there is recovered but about 90 per cent of the glycerol that is in the soap lye. Hence even after the glycerol is in the soap lye, there is a loss in its recovery.

With the continually advancing price of fats, oils, and other raw materials, it is becoming more necessary for the soap manufacturer to obtain a large glycerol yield; in fact it is essential that he should recover all the glycerol liberated by the saponification. Then, too, the grade of fats and oils obtainable for soapmaking is lower, because of increased utilization of the better grades for edible purposes, so that the soap manufacturer must strive to produce a good quality soap from a poorer grade of material.

The Krebitz process, here discussed, offers the possibility of recovering the theoretical yield of glycerol, while at the same time the caustic lime exercises some purifying action, especially in the case of a low-grade material. The Allen B. Wrisley Company, of Chicago, is the first in this country to work this process on a large scale with good results.

The Krebitz process is based on two simple chemical reactions:

In practice a batch of 10,000 lbs. of fat and oil may be conveniently handled. In a rather shallow tank 1200 to 1400 lbs. of lime are slaked with 3700 to 4500 lbs. of water, and the mass is heated, if necessary, to about 70° C. Then the fat and oil are run in while the entire mass is stirred vigorously. With live steam the mass is heated up slowly to 90–92° C., and taking about one-half hour to gain that temperature, with constant stirring, a thorough emulsion is obtained. The vessel is then covered to prevent loss of heat. Two or three hours after covering the mass is likely to boil and swell considerably. After it has stood 8

to 12 hrs., it has the appearance of a solid porous mass which is still sufficiently warm and soft to allow digging out the lime soap. This lime soap is dropped through a trap door in the bottom of the tank into a hopper and then to the mill where it is ground to the size of fine corn meal.

With the lime and water there will result between 15,000 and 16,000 lbs. of lime soap from 10,000 lbs. of fat and oil. The finely ground soap is carried on a conveyor and allowed to fall loosely into a circular, hopper-shaped tower, a capacity of about 25,000–30,000 lbs. being necessary. Four washes, about 40,000 lbs. of water, are required to leach out the glycerol from such a batch. The first wash water contains 10 to 12 per cent of glycerol, and is sent to the glycerin works. The second, third, and fourth waters are put on a fresh batch, only the last wash being made with fresh water. In this way, there is no cause for evaporating glycerin water containing less than 10 per cent of glycerol. When the plant is working satisfactorily the water evaporated averages 15 per cent of glycerol.

After the glycerol has been obtained, the lime soap is carried by a conveyor and introduced slowly into the soap kettle containing a boiling solution of soda ash. After the lime has been replaced by the soda, a stage which can be noticed by the nonappearance of small lumps on the paddle, a small amount of caustic soda is added, and shortly after the soap is salted out. The contents of the kettle are allowed to rest, when $CaCO_3$ settles out at the bottom as a heavy sludge, and the soap gathers on top, a salt solution containing an excess of alkali forming an intermediate layer.

Although Krebitz claims that the lime sludge will settle out and occlude or entangle but 4 to 7 per cent of soap, it has been impossible, so far, to prevent the occlusion of less than 9 to 12 per cent of soap. Of course, this soap must be recovered. At first this constituted quite a serious problem, because the lime sludge could not be filtered without leaving 2 to 3 per cent of soap in the lime cake. Attempts to wash out the soap by a series of washings and filtration were unsuccessful, because so much soap was present as to fill up the pores of the filter cloth, making filtration slow and unsatisfactory. Attempts to boil up the sludge with a little water and resalt out the soap were unsuccessful, because on salting out, the lime sludge settled to the bottom carrying most of the soap with it again. By continued experiment, it was found that the addition of enough water with heat and vigorous agitation caused the soap to go into solution, and on allowing the mass to settle the lime sludge, occluding but 3 to 5 per cent of soap, went to the bottom, the soap rose to the top, and could be pumped off and so recovered. The lime sludge could then be easily filtered, and only 1 to 1.5 per cent of soap is lost in the lime cake. This loss, though small, may perhaps still be reduced.

The quality and color of the finished soap obtained

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by the Krebitz process compares favorably with the soap produced by any other process. The amount of lime found in the finished soap depends on the number of washes or changes made in the kettle. Usually there was never less than 0.2 per cent of lime and it may run as high as 0.5 to 0.7 per cent lime. The process, however, claims that only a few thousandths of one per cent should remain in the finished soap.

At the present time a yield of about 95 per cent glycerol is being obtained by this process. This, compared to the yield of 60 to 80 per cent obtained by the recovery of glycerol from the soap lye in the case of soapmaking by boiling the glycerides with caustic soda, would give the Krebitz process a decided advantage. Moreover, we must recall that soap lyess contain at best but 5 to 8 per cent glycerol, depending on the way in which the changes of soap lye are worked up, and at the same time hold in solution much common salt, some caustic soda, soda ash, and organic impurities; whereas the Krebitz waters contain 12 to 15 per cent glycerol and are comparatively free from impurities, thereby making purification more simple and giving less water to handle and evaporate. Soda ash is cheaper than caustic soda, and since soda ash is used in place of caustic soda another material saving is made.

Without doubt, the Krebitz process would be preferred at this time, because of the high price of glycerol, but were glycerol 15 to 20 cents per lb. instead of 55 to 60 cents per lb. there might be a shadow of doubt as to whether it would be preferred to the soap-lye process taking into consideration the manifold operations prior to the soapmaking proper, and the work necessary to recover all the entangled soap from the lime sludge.

5872 NINA AVENUE
NORWOOD PARK, CHICAGO

THE DETERMINATION OF BENZOL IN COKE-OVEN GAS BY BURRELL'S VAPOR APPARATUS

By LOUIS C. WHITON

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The method for determining benzol and its homologues in gas as proposed by the Laboratory of Gas Investigations, U. S. Bureau of Mines,¹ has been tried in this laboratory with a view to determining the efficiency of benzol scrubbers utilizing coke-oven gas. The extraction of benzol, toluol and solvent naphtha has become at once such a profitable and important addition to a by-product coke oven's equipment that a rapid method of determination of scrubber efficiency seems imperative. The customary method of absorption of the vapors requires from 12 to 24 hrs. time and in this period many dollars worth of benzol and toluol may be lost, due to faulty operation of the scrubbers. Furthermore, especially when starting up a plant, conditions may have automatically been improved, without the operator's knowledge, toward the end of the test, which would mean that a change in operation as indicated by the test would perhaps be a disadvantage rather than otherwise.

The method as described in THIS JOURNAL did

¹ THIS JOURNAL, 7 (1915), 669.

not give the details of operation, which are extremely essential if accuracy is to be expected when determining such small traces of benzol vapors as are contained in debenzolized coke-oven gas.

Briefly, the apparatus as described by Burrell and Robertson, of the Bureau of Mines, consists essentially of a bulb about 6 in. long with a slight constriction in the center. The upper portion of the bulb contains glass wool mixed with phosphorus pentoxide to extract all the moisture from the gas. Connected with this bulb is a mercury manometer and an entry and exit tube with a ground glass 3-way cock. The air is first evacuated by means of a vacuum pump, the gas to be tested is sucked in and the 3-way cock turned when the gas is under barometric pressure. The entire bulb is then placed in liquid air or in a mixture of CO₂-snow mixed to a consistency of slush with alcohol or acetone. It is allowed to remain there 10 min., the temperature being approximately -78° C. The benzol freezes out at this temperature and the CO₂, O₂, CO, H₂, CH₄, N₂, and C₂H₄, which have a high vapor pressure at this temperature, are evacuated by means of the vacuum pump, the cock turned to seal the system and the apparatus brought up to room temperature. The partial pressure of the benzol vapor is registered on the manometer and this result divided by the barometric pressure times 100 indicates the per cent benzol.

There were several difficulties which had to be overcome in order to term the above a practical method for commercial work.

1—The readings on the manometer ranged from 10 mm. for benzolized gas to 1 mm. for debenzolized gas. With an ordinary manometer it is difficult to read much closer than 1 mm., which was beyond an allowable error.

2—In a vertical position it was impossible to surround the apparatus with the CO₂-alcohol slush with economy in the use of the material which withal, as a commercial proposition, is expensive.

3—The P₂O₅ in the glass wool soon ceased to be a good dehydrator and with the suggested construction of the apparatus it was impossible to charge it again with P₂O₅.

These difficulties were overcome to a certain extent in the following manner:

I—The mercury manometer was connected by means of a short, heavy piece of rubber tubing and was placed at a 10 to 1 slant, *i. e.*, 10 on the hypotenuse to 1 of altitude. This was placed on a firm gauge stand and leveled with spirit levels both ways. The gauge then gave a reading ten times the actual pressure. Thus it was possible to determine the pressure within 0.1 mm. which was sufficiently accurate.

II—The bulb was laid horizontally in a trough with a notch at the end through which the stem of the apparatus could pass. In this position it could be more easily surrounded with carbon dioxide slush without danger of breakage of the bulb and with greater economy in respect to the slush. This trough was 8 in. long, 2½ in. deep and 2½ in. wide, with a hinged cover and double walls with the air evacuated. It was