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In alcohol systems the pH is only a relative term; however it is a repeatable measurement even if not a "true" one. The slope at the end-point for the blank in the ethyl alcohol-solvent system represented by the broken-line curve in Figure 2 is 0.037 and for the sample of the saponified linseed oil at the phenolphthalein end-point the slope is 0.308. The normal good break in the curve when titrating a strong base with a strong acid is observed. The curve is flatter and covers a much narrower pH range in the titration of the salt of the weak acid obtained by saponification.

Figure 2 adequately explains the difficulty in obtaining a precise end-point with an indicator in the n-butyl alcohol system. The solid line curve for the blank depicts titration of n-butyl alcoholic alkali in water with aqueous hydrochloric acid. The peculiar hump near the end-point is rather disturbing, and no adequate explanation is available. Possibly the inflection could be caused by the immiscibility of butyl alcohol and water in that at the breaking point or end-point the last traces of free potassium hydroxide have to be extracted by the water from the butyl alcohol. This may be a slow process, causing the indicator to fade and at the same time causing the pH to change only slightly on addition of acid. It was thought that this condition could be corrected by the simple addition of a water-butyl alcohol miscible solvent such as ethyl alcohol. By inspection of the dotted-line curve it can be seen that this was partially accomplished. However, the results, though corrected somewhat, leave much to be desired as the slope for the blank is 0.282 and for the sample, 0.658. Compared to the obtained slopes of 0.037 and 0.308, using ethyl alcohol-water as titration media, it can be readily seen that a relatively slight error in titration could cause appreciable errors in the results.

Conclusions

The use of n-butyl alcohol as a solvent for saponification of a representative series of drying oils has been studied. It appears from this work that n-butyl alcoholic potassium hydroxide reagent, containing 5% of water added to the reaction mixture, gives very acceptable results based upon calculated saponification values.

With the exception of maleic-modified oils of certain types, the solvent system of ethyl alcohol-pyridine exhibits excellent results based upon calculated values. However it has the disadvantages that it is a two-solvent system, and the pyridine must be of reagent grade to avoid end-point difficulties.

The end-point in the butyl alcohol system is not as sharp as the normal saponification end-point in ethyl alcohol. This may be caused by the two-phase nature of the titration mixture. Addition of ethyl alcohol to the n-butyl alcoholic saponification reaction mixture gives improvement, although the end-point is not as sharp as in the regular ethyl alcohol system. Work is continuing on methods for improvement of the end-point.

REFERENCES


Simultaneous Recovery of Wax and Oil From Rice Bran by Filtration-Extraction

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Manufacturers of wax preparations for home and industrial uses in this country are interested in obtaining new sources of hard vegetable waxes other than carnauba. For the year 1951 the United States imported 26,340,000 pounds of vegetable waxes valued at $21,082,000, the largest part being carnauba, 16,016,279 pounds worth an average price of $0.929 per pound (11). Potentially rice bran is a source of hard vegetable wax. Rice bran contains a percentage range of lipids which are about 14 to 17% oil (8) of which 3 to 9% is wax. The yield of the total available lipids and the oil-wax relationship will be dependent upon the solvent temperature.
conditions, source and history of the bran, and other factors (10). On the bran basis this is equivalent to 0.4 to 1.5% crude wax. Only a part of this is a hard wax fraction having a melting point of 75.3 to 79.9°C (2). Based on a yield of 0.25% of hard wax from rice bran, a 100-ton per day rice bran solvent extraction plant would produce approximately 500 pounds of wax having a value of $188 to $375. This means, in addition to the value of oil and meal products, an added revenue of $46,875 to $93,750 for a 250-day processing year.

Previous publications have reported experimental methods and yields for the solvent extraction of wax from rice bran or oil, as well as data on the properties of the extracted wax (1, 2, 6, 7, 10, 13). These methods employed solvents other than hexane, which is used commercially to extract the rice oil. For commercial application it is desirable to have a method requiring only a single solvent to produce separately both oil and wax from the bran. Pilot plant extractions of rice bran (10) and observed settling of wax from rice oil-hexane miscellas at low temperatures (3) at the Southern Regional Research Laboratory led to this investigation of rice wax preparation from hexane solutions. Hard, high melting point rice waxes were prepared from rice bran by two methods: 1. selective cold hexane extraction to remove oil, followed by a hot hexane extraction to remove the wax and chilling the wax miscella to precipitate the wax, or 2. a single hot extraction to remove both oil and wax, followed by the separation of wax from the miscella by chilling and multiple washes with cold hexane. Both methods were carried out on a pre-pilot plant scale and were based on the principles of filtration-extraction (4, 12).

Materials and Equipment

Two lots of raw rice bran, designated as Nos. 1 and 2, were obtained from a rice mill in New Orleans. They had an oil content of 16.5-17.0% and a moisture content of approximately 10%. Portions of each were cooked in a five-high stack cooker and an Evarts K. Loomis mixer, respectively. The cooked materials were similar to each other. The cooking operations consisted essentially of heating the brans to a temperature of approximately 210°F., adding water or live steam to bring the moisture up to approximately 9.5% moisture (4).

Filtration-extractions were performed, using either a vacuum crock (12) or a metal cylinder (5) with a removable plain Dutch screen, 24 x 110-mesh. For the processing variables studied, the rice brans were slurried with an 8% oil miscella and the washes, containing 2%, 1%, and 0% oil, respectively. Additional extractions and washes after the cold extractions were made with hexane. In the wax preparations only hexane was used in the slurring and washing operations.

Processing Variables Studied

Effect of Temperature on Solvent Extraction of Wax from Rice Bran. Laboratory filtration-extractions with hexane as a solvent were made on cooked rice bran to determine the effect of temperature on the extraction of acetone insoluble lipids1 or total wax as shown in Figure 1. At 155°F, 93.0% of the total wax was extracted and at 41°F, 42.5%. Acetone insoluble lipids were used as an index for the wax content of rice bran as waxes are generally insoluble in acetone. Low acetone insoluble lipids of a rice bran indicate low wax content. Since solvent extracted brans containing low residual lipids also contain relatively small amounts of acetone insoluble lipids, low residual lipids also indicate the extent to which wax extraction has taken place.

Cold Extraction. Effect of Filtration Factors on Residual Lipids. To determine the effects of the solvent-bran ratio, number of washes, and filtration time on residual lipids, filtration-extractions were made on cooked rice bran at a temperature of approximately 40°F. Table I shows that slower rates on filtration did not decrease residual lipids; as the solvent-bran ratio decreased, residual lipids increased; and a change in the number of washes from three to two increased the residual lipids. Filtration-extraction of unslurried brans gave a residual lipids of 3.64% as compared to 2.40-2.82% for slurried material.

Hot Extraction. Effects of Temperature on Extraction of Cold Extracted Bran. Filtration-extractions were conducted on the cold solvent damp bran previously extracted at 40°F. Table II shows data obtained on the mass velocity and final residual lipids. The low lipids obtained indicate that the wax can be removed without reslurrying and high mass velocities indicated the practicability of filtration-extraction. A temperature as low as approximately 90°F. may be used to remove the wax in the hot solvent-extraction of cold solvent-extracted rice bran. The cold extracted bran can be brought up to temperature with two washes.

1To determine acetone insoluble lipids, residual lipids, A.O.C.S. standard method As 4-38 were treated with acetone at 78°F, transferred to a fritted filter with washings and dried in a vacuum oven at 105°F.