hydrochloric acid in contrast to the fairly good end-point in the ethyl alcohol or the ethyl alcohol-pyridine systems. Potentiometric titrations were made for the systems of ethyl alcohol-water, n-butyl alcohol-water, and n-butyl alcohol-ethyl alcohol-water.

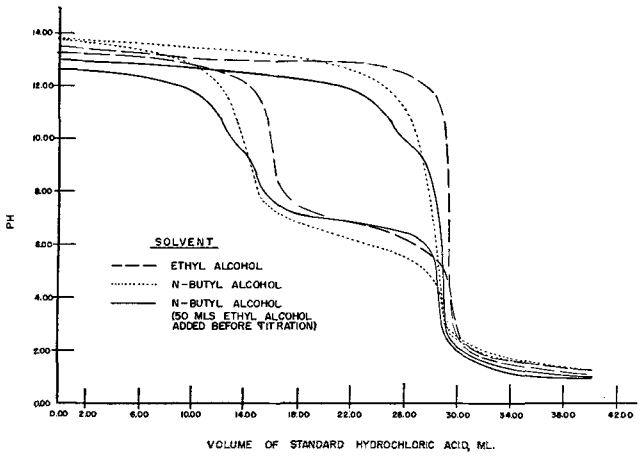

FIG. 2. Titration graph of saponified linseed oil.

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.

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Simultaneous Recovery of Wax and Oil From Rice Bran by Filtration-Extraction[1]

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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

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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[3] 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 19% and drying at the same temperature 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 contained 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 slurrying 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 lipids[4] 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

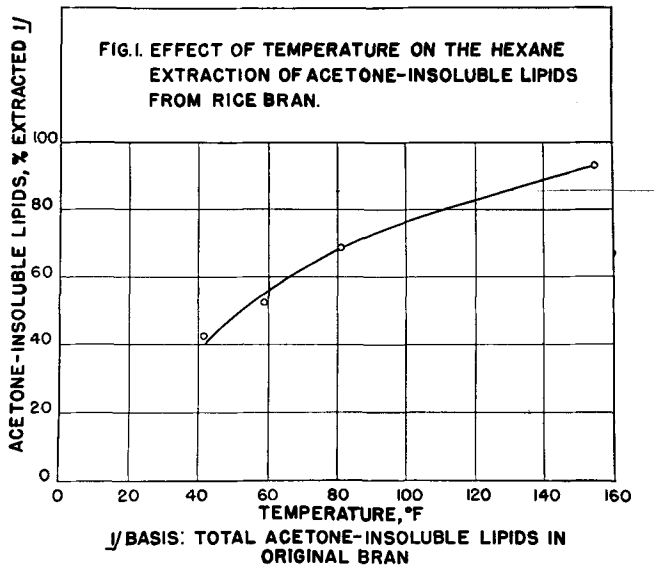

FIG. 1. Effect of temperature on the hexane extraction of acetone-insoluble lipids from rice bran.

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.

[3] In using the names of equipment manufacturers in this article, it should be understood that we are not recommending the products of one manufacturer over similar products of another manufacturer.

[4] To determine acetone insoluble lipids, residual lipids, A.O.C.S. standard method Aa 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.

TABLE I

Effects of Solvent Meal Ratio, Number of Washes and Time on Residual Lipids in Cold Filtration Extraction of Rice Bran

Experiment	1	2	3	4	5	6
Condition	Control fast rate	Fast rate	Medium rate	Slow rate	Fast rate	Fast rate
Wt. meal, g.	360	360	360	360	360	360
Solvent meal ratio	1.3:1	1.3:1	1.3:1	1.3:1	1.1:1	0.75:1
Slurry						
Time, min	30	34	30	31	30	30
Temp. °F	39	40	43	44	39	41
No. washes	3	2	2	2	2	2
Wash temp. °F	39	40	37	37	39	39
Mass velocity lbs./ft.²/hr.	2,416	1,940	966	455	2,220	2,015
Extracted cake						
Final temp. °F	44	44	44	43	45	44
Lipids, M.F.B.,[a] %	2.03	2.61	3.03	2.66	3.03	3.52

[a] Moisture free basis.

Wax Production

Based on the data obtained on the above processing variables, wax was produced by two methods. In Method No. 1 there was a preferential cold hexane extraction of rice bran to remove the oil followed by a hot hexane extraction to remove wax. The wax miscella was cooled to approximately 40°F., and the precipitated wax was recovered by centrifugation. In Method No. 2 a single hot solvent-extraction of rice bran was employed to remove simultaneously the oil and wax. Wax was separated from the oil and wax miscella either directly or after a hot water washing of the miscella, by chilling, settling or centrifuging, and desolventizing. Results of four preparations of wax from rice bran are given in Table III. The first preparation follows Method No. 1, and the other three, Method No. 2.

Preparation No. 1. Essentially all the oil from 24.6 lbs. of cooked rice bran was removed with cold hexane (40°F.) at a solvent to bran ratio of 1.3 to 1 in the vacuum crock filtration-extraction system (12). The filtrates passed through the bran cake at an average mass velocity of 2,875 lbs./sq. ft./hr. The extracted bran had a residual lipids content of 1.36%. Portions of the extracted-solvent damp bran were reslurried with hot hexane at 140°F. for 30 minutes, filtered, and then washed with hot hexane, using a solvent to bran ratio of 1.3 to 1. The hot wax miscella had a mass velocity of 1925 lbs./sq. ft./hr. The extracted meal had a lipids content of 0.24%.

The hot wax miscella was filtered and cooled to 40°F., forming a wax precipitate equal to approximately 1% of the total volume. The precipitated wax which contained 29.1% solids was recovered by centrifugation at a relative centrifugal force of 880 in a refrigerated centrifuge. The centrifuged wax was air-dried to remove completely the hexane, and the dried wax was melted and cooled to form a solid mass.

Preparation No. 2. Five lbs. of cooked rice bran No. 1 was slurried at approximately 150°F. for 30 minutes and then filtered in the metal cylinder filtration-extraction test unit (5), using four hexane washes at a temperature of approximately 150°F. The solvent to bran ratio was 2 to 1 for the slurrying operation and 1.3 to 1 for the four washes. The resulting miscella, containing both the oil and wax, was concentrated to an oil content of approximately 70%. The wax was precipitated from the concentrated oil miscella by chilling it to 40°F. The wax was recovered by centrifuging in a manner identical to that used in Preparation No. 1. The crude wax was purified by three successive precipitations. Each consisted of redissolving the wax at 150°F., chilling to 40°F. and centrifuging, using three, four, and five volumes of hexane, respectively, for the three precipitations. The centrifuged purified wax fraction was air-dried, melted, and cooled to form a solid hard mass. Table III shows that the wax yield for this preparation was similar to that for Preparation No. 1.

Preparations 3 and 4. Wax was recovered from 31 lbs. of raw bran No. 2 and from the same quantity of cooked bran No. 2 in Preparations Nos. 3 and 4, respectively. The same extraction equipment was used in these preparations as for Preparation No. 2, but the extraction procedure differed in that each bran was slurried with 1.5 times its weight of 150°F. hexane and then filtered. In a like manner the filtered bran was reslurried and then filtered. These operations were repeated a third time, for a total of three consecutive extractions. The three filtrates were

TABLE II

Hot Hexane Extraction of Cold Hexane Extracted Bran

Cold Extraction				Hot Extraction[a]					
Extraction temp.	Washes	Mass velocity	Extracted bran analyses	Reslurry	Extraction or wash temp.	Washes	Final cake temp.	Mass velocity	Re-extracted bran analyses
			lipids M.F.B.[b]						lipids M.F.B.[b]
°F.	No.	lbs./ft.²/hr.	%		°F.	No.	°F.	lbs./ft.²/hr.	%
41	2	2,555	2.77	No	145	2	131	4,040	0.56
				No	158	3	135	3,480	0.42
				Yes	136	3	133	3,850	0.27
39	3	2,875	1.47	No	91	3	87	1,470	0.39
				No	142	3	131	1,840	0.19
				No	154	3	142	1,580	0.27
				Yes	147	3	137	2,230	0.13
				Yes	140	2		1,900	0.28

[a] Meal at 40°F. when extracted with hot solvent.
[b] Moisture free basis.

TABLE III

Wax Preparation, Data, and Results

Preparation No.	Rice bran material	Bran Analyses			Wax			
					Yield		Analyses	
		Bran No.	Lipids M.F.B.[a] %	% Total acct. insol. lipids extracted[b]	Bran basis M.F.B.[a] %	Extr. oil basis %	Melting point °C.	Phosphorus %
	Method 1—Cold Solvent Extraction Followed by Hot Solvent Extraction							
1	Cooked, unextracted	1	18.56					
	Cooked, extracted cold		1.49					
	Cooked, extracted hot		0.27	94.3	0.28	1.50	78.4	1.4
	Method 2—Hot Solvent Extraction							
2	Cooked, unextracted	1	18.55					
	Cooked, extracted		0.71	94.5	0.28	1.48	78.8	0.53
3	Raw, unextracted	2	18.37					
	Raw, extracted		0.85	93.3	0.34	1.82	78.4	0.14
4	Cooked, unextracted	2	18.61					
	Cooked, extracted		0.30	91.4	0.24	1.29	80.0	0.13

[a] Moisture free basis.
[b] % total acetone insoluble lipids extracted. Basis: Total acetone insoluble lipids in unextracted meal.

combined and then water washed for 30 minutes with approximately 10% water at a temperature of approximately 140° F. to remove some phosphatides. After the miscella was separated from the water portion, it was cooled to 40°F. to precipitate the wax. The precipitated wax was purified by resuspending it three times with five volumes of hexane at 40°F. The purified, settled wax was desolventized, melted, and cooled to form a solid mass. Filtration rates of miscella through raw rice bran were too slow for practicality. It was noted that the water washing prior to cooling of the miscella improved the separation characteristics of the wax. Hot water washing the miscella from the raw bran removed 3.2 g. of crude phosphatides with a 1.68% phosphorous content. This decreased the amount of phosphorous in the final wax. The yield of wax from the raw bran was greater than that from the cooked bran. All four preparations produced hard waxes with high melting points, ranging from 78.4 to 80°C. In Table III acetone insoluble lipids of the extracted brans indicate that the extent of wax removal was nearly equal for the four preparations. This is not indicated by the lipids values.

For comparative purposes settlings from a commercial solvent-extracted raw rice bran oil were dissolved in hot hexane, and the resulting miscellas were treated for wax separation in a manner similar to that used in Preparations Nos. 3 and 4. The final wax produced was equal in hardness and melting point to the other rice waxes.

Oil Evaluation. The oil miscellas from Preparations Nos. 1, 3, and 4 were concentrated and steam-stripped to remove solvent and then vacuum-dried to remove moisture. The crude oils were refined and bleached by a modified A.O.C.S. method as described by C. H. Pominski *et al.* (9), and results are reported in Table IV.

For comparison with the oil obtained from Preparation No. 1 (cold and hot extractions) composite samples of the mixed and settled oils prepared in the pilot plant by filtration-extraction of rice bran (cooked bran No. 1) at 85°F. (4) were refined and bleached by the same method. The settled oil from the pilot plant operation gave the lowest refining loss; however the oil from the cold extraction (Preparation No. 1) gave a lower loss than that obtained from the unsettled oil.

The refining loss of the oils obtained in Preparations Nos. 3 and 4 (straight extraction of raw and cooked rice bran) showed no improvement over high losses normally expected from solvent-extracted rice oils.

Discussion

These investigations show that a hard, non-tacky rice wax can be produced by one of two methods which use a single solvent (hexane) and simulta-

TABLE IV

Rice Oil Refining and Bleaching Data

Wax preparation	Bran No.	Oil	FFA %	Refining Data			Lovibond Color	
				Lye %	Lye excess %	Refining loss %	Refined Oil[a] (70Y) Red	Bleached Oil[b] (35Y) Red
	Pilot Plant Extraction							
....	1 cooked	Extracted room temperature, mixed	2.90	14	0.5	20.0	2.3	3.8
				16	0.5	22.0	2.3	
....	1 cooked	Extracted room temperature, settled	2.75	14	0.5	12.6	2.7	3.8
				16	0.5	13.5	2.7	
	Method 1—Cold Solvent Extraction Followed by Hot Solvent Extraction							
1	1 cooked	Extracted, cold	3.24	14	0.5	15.3		
				16	0.5	14.8		
				16	0.5	15.4	2.3	3.2
	Method 2—Hot Solvent Extraction							(70Y)
3	2 raw	Extracted hot, water washed	6.20	14	0.5	27.2	3.2	6.6
				16	0.5	26.0	3.2	6.6
4	2 cooked	Extracted hot, water washed	3.26	14	0.5	23.5	2.3	2.7
				16	0.5	23.6	4.1	5.3

[a] 1″ of oil in color tube.
[b] 1% Nuchar and 5.6% official bleach earth.

neously produce oil. In the first method, which is preferable, the data indicate that if rice bran is cooked, both hot and cold solvent-extractions can be performed in a single extractor of the filtration-extraction type (4) since the filtration rates are high and within practical limits. This method has the advantage that no water- or solvent-washing is necessary to produce purified wax, and probably only one centrifuge would be necessary. Figure 2 shows a proposed flow diagram for a filtration-extraction process, without reslurring, to produce wax and oil from rice bran, based on this method.

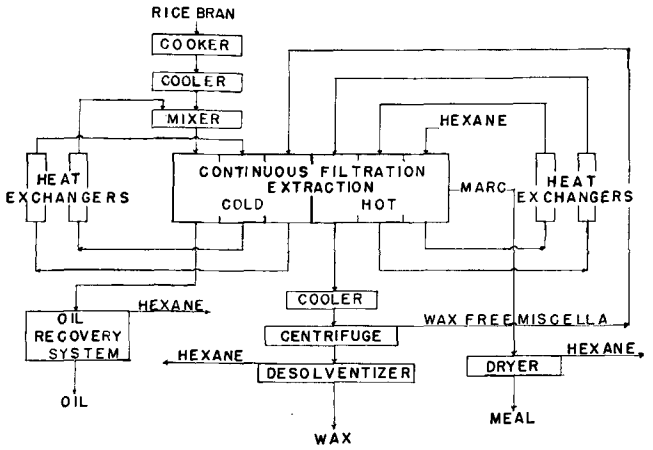

FIG. 2. Proposed flow diagram of filtration-extraction process for simultaneous production of rice wax and oil.

In the second method a multiple number of cold solvent-washes would be necessary after a hot water washing to purify the wax, and this would necessitate the use of a number of centrifuges. Figure 3 shows a proposed flow diagram for a solvent-extraction plant to produce wax and oil from rice bran based on this method (straight hot extraction). The flow diagrams shown in Figures 2 and 3 are only proposed processes, and future engineering research and development investigations are necessary to determine their commercial feasibility.

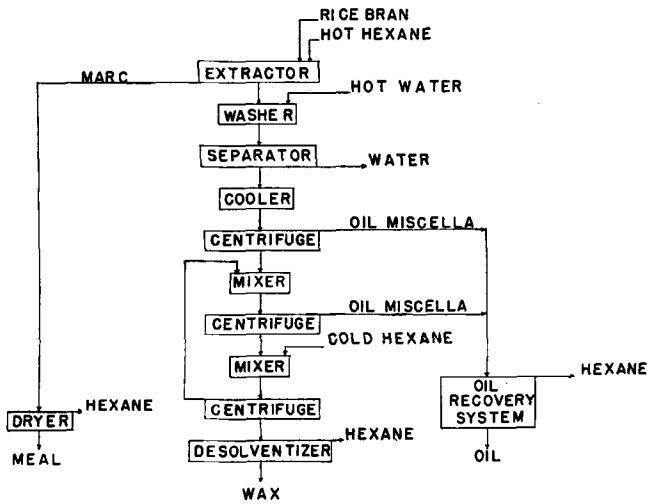

FIG. 3. Proposed flow diagram for simultaneous production of rice wax and oil by a single hot extraction.

If all acetone insoluble lipids at 40°F. are considered hard wax, then approximately 57% of the total acetone insoluble lipids may be considered as hard wax. On this basis the actual wax yield itself is 70% of the total hard wax.

Summary

Hard rice waxes of high melting points have been obtained directly from rice bran while simultaneously producing oil. These waxes were produced by the following two methods. 1. selective cold hexane-extraction of cooked rice bran to remove the oil, hot hexane-extraction to remove the wax, chilling of the hot miscella and separation of the precipitated wax by centrifugation; 2. single hot hexane-extraction of raw or cooked rice bran, hot water washing and chilling of the miscella, separation of the wax precipitate by settling or centrifugation, and multiple cold hexane-washings of the wax. Wax can also be processed from rice oil settlings by the latter method after a miscella has been prepared. The cold extraction-hot extraction method should be preferable as a process when conducted on a single continuous filtration-extraction unit without reslurrying. Indications are that oil refining losses may be decreased by this method. Yields of rice wax varied from 0.22 to 0.31% of the original rice bran, or 1.29 to 1.82% of the extracted oil.

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