ployed to precipitate the gums from crude fatty oils. Precipitation of the gums from the liquid propane solution of the crude oils occurred at about 70°C. and 350 lb./sq. in. pressure.

REFERENCES

1. Ewing, F., U. S. Patent 2,288,441.
2. Wilson, Keith, and Haylett, Trans. Amer. Inst. Chem. Engrs. *32*, 364-406 (1936).
3. Hixson, A. W., and Miller, R., U. S. Patent 2,247,496.
4. Hixson, A. W., and Hixson, A. N., Trans. Inst. Chem. Engrs. *37*, 927-954 (1941). Hixson, A. W., and Bockelmann, J. B., Trans. Inst. Chem. Engrs. *38*, 891-930 (1942).
5. Drew, D. A., and Hixson, A. N., Trans. Inst. Chem. Engrs. *40*, 675-694 (1944).
6. Reference 4, page 931.

[Received August 8, 1949]

Rice Bran Oil. V. The Stability and Processing Characteristics of Some Rice Bran Oils[1]

C. E. SWIFT, SARA P. FORE, and F. G. DOLLEAR, Southern Regional Research Laboratory,[2]
New Orleans 19, Louisiana

DATA and information have been presented in the previous reports of this series on the extraction and processing (1), composition (2), and utilization (3), of rice bran oil produced from several varieties of Southwestern-grown rice brans and on the effect of storage of the bran on the free fatty acid content of the extracted oil (4). The present report is an extension of previous work to include data on nine different lots of rice bran as well as data with reference to the stability of unhydrogenated and hydrogenated oils.

Extraction of Crude Oils

One sample each of freshly milled bran from Rexoro, Patna, and Magnolia varieties and two batches of bran from Zenith variety of rice were obtained from a local rice mill and subjected within a few hours to solvent extraction. Each lot of 360 pounds of bran was extracted with a total of 500 gallons of hexane at prevailing atmospheric temperature in a previously described extractor (5). The miscellas were concentrated by evaporation at approximately 65°C. After standing several days the separated solids were removed by filtration. Data and information with respect to the variety, lipid, and moisture content of the brans (A to E, inclusive) as well as the yield, color, and content of free fatty acids of the corresponding crude oils are given in Table 1.

Three 10-pound batches of bran (F to H, inclusive) produced from "Converted" rice shipped from Houston, Texas, were extracted in a large glass Soxhlet-type extractor. A fourth 10-pound batch of bran produced locally from Blue Rose variety of rice (I) was similarly extracted. The contents of free fatty acids of the rice bran oils, F to I, were 4.7, 2.1, 2.0, and 2.9%, respectively.

Extraction in the pilot plant of the five batches of bran containing from 13.8 to 17.0% hexane-soluble lipids yielded crude oils approximately equivalent to 91% of the hexane-soluble lipids present in the bran (Table I). Subsequent re-extraction of these brans with hot hexane yielded only semi-solid materials, indicating that the original extraction in the pilot plant had removed practically all of the glycerides. The crude oils obtained in pilot plant extractions contained 3.0 to 6.3% free fatty acids even though the freshly milled bran was extracted within a few hours after milling. By comparison the brans produced from "Converted" rice and shipped from Houston, Texas, to New Orleans gave crude oils (F to H) containing 4.7, 2.1, and 2.0%, respectively, thus indicating that the treatment (6) followed in the "Conversion" process markedly inhibits hydrolysis of the oil in the bran.

Refining and Bleaching

The nine crude oils (A to I, inclusive) were refined according to the procedure of the Official and Tentative Methods of the American Oil Chemists' Society (7) prescribed for slow-break cottonseed oil (Method Ca 9a-41) except that the lye used was 0.5% excess of the quantity required to neutralize the free fatty acids. The refined oils were bleached according to the directions for bleaching refined cottonseed oil (Method Cc 8a-47). The content of neutral oil in crude oils (A to F, inclusive) was determined by the method described by Jamieson (8). Results of the refining and bleaching tests are shown in Table II.

TABLE I

Characteristics of Rice Bran and Oils

Samples	Bran				Crude Oil					
	Variety of rice[1]	Locality grown	Hexane-soluble lipids, per cent	Moisture, per cent	Yield,[2] per cent	Free fatty acids, per cent	Lovibond color			
							1″ column		5¼″ column	
							Y	R	Y	R
A	Rexoro	Eunice, La.	13.8	10.8	90.5	3.0	....	....	70	13.1
B	Patna	Vinton, La.	14.9	10.6	92.6	3.1	70	5.6	....	....
C	Zenith	Knable, Ark.	17.0	11.6	91.0	3.0	....	....	70	12.7
D	Zenith	Rayne, La.	15.9	11.0	91.0	4.9	70	4.6	....	....
E	Magnolia	Eunice, La.	16.4	11.8	90.5	6.3	70	4.2	....	....

[1] Field dried. [2] Yield, per cent $= \frac{\text{weight oil recovered from miscellas}}{\text{weight bran extracted} \times \text{original content of hexane-soluble lipids (per cent)}} \times 100.$

---

[1] Presented at the 40th Annual Meeting of the American Oil Chemists' Society, New Orleans, La., May 10-12, 1949.

[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

TABLE II

Refining Characteristics of Rice Bran Oil

Sample	Free fatty acid, per cent	Neutral oil,[1] per cent	Refining [2]		Lovibond color			
					5¼″ column			
			Lye, °Bé	Loss, per cent	Refined oil		Bleached oil [3]	
					Y	R	Y	R
A	3.1	92.0	16	13.6	70	7.2	15	1.5
B	3.4	92.6	12	12.6	70	6.0	35	2.3
C	3.0	91.5	14	16.1	70	6.7	35	3.2
D	4.9	89.9	16	20.5	35	7.5	35	2.9
E	6.3	89.9	12	23.5	70	5.6	35	2.6
F	4.7	92.2	14	19.6	70	6.7	35	2.3
G	2.1	......	16	16.8	35	4.5	20	2.8
H	2.0	......	12	12.0	70	4.9	35	2.7
I	2.9	......	16	13.5	70	9.5	35	2.9

[1] Determined by the method described by Jamieson (8).

[2] Refined by Official A.O.C.S. Method Ca 9a-41 (7), for slow-break cottonseed oil using 0.5% excess lye.

[3] Bleached by Official A.O.C.S. Method Cc 8a-47 (7).

The refining losses were slightly higher than those calculated for cottonseed oil containing the same percentages of free fatty acids by means of the following formulas: per cent refining loss = 4.25 + 2.3 (per cent FFA) (9); or per cent refining loss = 4.0 + 2.1 (per cent FFA) (10). No difficulty was encountered with respect to coalescence of the soap stock although they were soft and contained unrecoverable neutral oil. Since the centrifugal caustic soda (11) and soda ash (12) processes produce refining losses more nearly approaching the Wesson loss than is the case with the cup method, it is possible that the bulk of the neutral oil content of oils (A to E, inclusive) ranging from 89.9 to 92.6% would be recoverable in plant refining operations. The Lovibond color of the refined oils ranged from 35 yellow and 4.5 red to 70 yellow and 9.5 red, and the color of bleached oils ranged from 15 yellow and 1.5 red to 35 yellow and 3.2 red. The refined and bleached rice bran oils were therefore as light or only slightly darker than the maxima specified in the Trading Rules of the National Cottonseed Products Association (13) for Prime Summer Yellow (35 yellow and 7.6 red) and Bleachable Prime Summer Yellow (20 yellow and 2.5 red) cottonseed oils.

The applicability of degumming prior to refining was investigated by passing steam through crude rice bran oils A, C, D, and E for 15 minutes after which the oils were filtered, refined, and bleached. The results of these refining and bleaching tests are shown in Table III, together with corresponding data for refining and bleaching the original crude oils.

The losses in refining the degummed oils were 1.3 to 1.9% lower than those obtained on the original crude oils. However the small reductions in refining losses would not warrant degumming unless it were practiced for the recovery of phosphatides. As shown in the data in Table III, the refined and bleached oils produced from the degummed oils and the original crude oils had approximately the same color.

TABLE III

Comparison of Refining Crude and Degummed Rice Bran Oil

Samples	Free fatty acids, per cent	Refining [2]		Lovibond color			
		Lye, °Bé	Loss, per cent	Refined oil		Bleached oil [3]	
				Y	R	Y	R
A	3.1	16	13.6	70	7.2	15	1.5
A (degummed)[1]	3.1	16	11.9	70	8.1	20	2.7
C	3.0	14	16.1	70	6.7	35	3.2
C (degummed)	3.0	14	14.8	35	7.2	35	3.7
D	4.9	16	20.5	35	7.5	35	2.9
D (degummed)	5.0	14	18.6	70	7.8	35	3.4
E	6.3	12	23.5	70	5.6	35	2.6
E (degummed)	6.3	12	21.6	35	4.5	20	1.7

[1] Steam was passed into samples for 15 minutes after which the oils were filtered.

[2] Refined by Official A.O.C.S. Method, Ca 9a-41 (7) for slow-break cottonseed oil using 0.5 per cent excess lye.

[3] Bleached by Official A.O.C.S. Method Cc 8a-47 (7).

The value of refining rice bran oil by a combination of steam- and alkali-refining methods was investigated. Steam refining was accomplished in an apparatus ordinarily used for laboratory deodorizations (14). Only degummed oils were steam-refined since preliminary tests indicated that rice bran oil becomes practically unbleachable if it is not degummed prior to steam-refining. A test of combined steam- and alkali-refining with a degummed oil (Sample E) was made as follows: 600 g. of degummed oil was steam-refined for 2 hours at 1-2 mm. and 250°-260° C. using steam equivalent to 6% of the weight of the oil. The free fatty acid content of the oil was reduced from 6.3 to 0.5%, and the weight of the oil was reduced 7.8%. The steam-refined oil was refined with 7.1% of 12° Bé lye with a refining loss of 6.6%. The total loss occurring by steam- and alkali-refining was calculated by means of the formula: steam refining loss + (100 − steam refining loss) × alkali refining loss = total refining loss. The steam refining loss of 7.8% and the alkali refining loss of 6.6% were substituted in the formula, and it was calculated that the total loss was 13.9% compared with a loss of 21.6% obtained by refining the degummed oil with alkali only (degummed oil E, Table 3). The steam- and alkali-refined oil when bleached with 4% activated earth (A.O.C.S.) had a color of 35 yellow and 2.4 red Lovibond units. The results indicate that a combination of steam- and alkali-refining would be economical especially for refining rice bran oil containing appreciable free fatty acids.

Stability

A series of finished rice bran oils was prepared by deodorizing the previously described refined and bleached oil (A to I, inclusive) for one hour at 210° C. in a laboratory deodorizer (14). Batches of 200 g. each of the series of refined and bleached oils were hydrogenated in a Parr Model CA hydrogenator at 150°C. and 20-40 p.s.i., using a catalyst which contained 0.2 g. of active nickel. The following characteristics were determined for these products: the iodine values of both the original and hydrogenated oils, the micropenetration values of hydrogenated oils at 25°C. (15), and the stabilities of the refined, bleached, and deodorized oils and the hydrogenated oils by the active oxygen method at 97.7°C. These data are shown in Table IV.

The refined, bleached, and deodorized oils had iodine values ranging from 101.3 to 105.7 and averaging 103.8. The stabilities ranged from 20 to 29 hours and averaged 24 hours. The hydrogenated oils had iodine values ranging from 65.4 to 66.6 and micropenetration values at 25°C., which ranged from 41 to 110 mm. and averaged 71 mm. The stabilities of the hydrogenated products ranged from 225 to 460 hours and averaged 370 hours. The stabilities of the refined, bleached, and deodorized rice bran oils and of the hydrogenated products were approximately twice those of comparable commercially acceptable vegetable fats.

TABLE IV

Stability of Unhydrogenated and Hydrogenated Rice Bran Oils

Sample	Refined, bleached, and deodorized		Hydrogenated Oil[1]				
	Iodine value Wijs method	Stability, A.O.M., hours	Iodine value Wijs method	Micro-penetration, 25° C., mm.	Lovibond color 5¼" column		Stability A.O.M. hours
					Y	R	
A	103.7	24	66.6	88	10	1.7	415
B	105.7	24	65.6	77	15	2.4	300
C	105.2	22	66.3	110	15	1.8	375
D	101.9	21	65.4	69	15	1.4	415
E	102.3	29	65.7	....	....	....	......
F	104.3	29	65.9	41	10	1.7	460
G	104.8	20	65.9	41	10	1.2	350
H	103.5	20	65.5	68	10	1.2	435
I	101.3	29	65.4	74	20	2.6	225
Average	103.8	24	65.8	71	....	....	370

[1] Refined and bleached oils hydrogenated at 150°C., 0.1 per cent nickel catalyst, 20-40 pounds pressure, deodorized 1 hour at 210°C.

Flavor Stability

The flavor stabilities of refined, bleached, and deodorized rice bran oils, D and E, were investigated to ascertain if the oils were subject to reversion. The oils were deodorized for two hours at 210°C. and 1-2 mm. pressure. The bland oils were placed in beakers at room temperature, exposed to light from a window on the north side of the laboratory, and examined periodically by three individuals. Flavors described as grassy, cardboard-like, and oily developed in oils D and E after 2 and 15 hours, respectively. The character of the flavors which developed and the absence of any evidence of rancidity in the samples indicated the occurrence of flavor reversion. One-tenth per cent citric acid was added to one of the refined and bleached oils (Sample E) and the oil deodorized as before. The bland product was stored for 40 hours in an open beaker before any off-flavor was detected.

No tendency towards reversion in hydrogenated rice bran oil was detected in tests which involved heating the hydrogenated oils to near the smoke point and cooling to room temperature. The results suggest that rice bran oil can most advantageously be utilized in the form of a hydrogenated product of unusually high stability.

Summary

1. The extraction, processing, characteristics, and stability properties of nine batches of hexane-extracted rice bran oil were investigated. The oils were refined, bleached, and deodorized and their color and stability determined. Samples of the bleached oils were hydrogenated to approximately shortening consistency, deodorized, and the stability of the hydrogenated products determined.

2. Pilot plant extractions of five batches of rice bran yielded crude oils equivalent to 91% of the hexane-soluble portions of the bran.

3. The nine crude oils whose content of free fatty acids ranged from 2.0 to 6.3% were refined by the cup method with losses ranging from 12.0 to 23.5% although the neutral oil content of six crude rice bran oils ranged from 89.9 to 92.6%.

4. The Lovibond color of the nine refined oils ranged from 35 yellow and 4.5 red to 70 yellow and 9.5 red, and the color of the bleached oils ranged from 15 yellow and 1.5 red to 35 yellow and 3.2 red.

5. Steam-refining, employed in conjunction with alkali-refining, proved effective as a means of reducing the losses in refining rice bran oil.

6. The nine batches of refined, bleached, and deodorized rice bran oils had iodine values ranging from 101.3 to 105.7 and stabilities averaging 24 hours.

7. Nine bleached oils hydrogenated to approximate shortening consistency had iodine values averaging approximately 66 and stabilities averaging 370 hours.

8. Refined, bleached, and deodorized rice bran oil is bland but has some tendency toward flavor reversion.

9. The most outstanding characteristic of rice bran oil is its exceptional stability after hydrogenation.

Acknowledgment

The authors wish to express their appreciation to the Engineering and Development Division of this Laboratory for the pilot plant extraction of the rice bran oils used in this investigation.

REFERENCES

1. Reddi, P. B. V., Murti, K. S., and Feuge, R. O., J. Am. Oil Chem. Soc., *25*, 206-211 (1948).
2. Murti, K. S., and Dollear, F. G., J. Am. Oil Chem. Soc., *25*, 211-213 (1948).
3. Feuge, R. O., and Reddi, P. B. V., J. Am. Oil Chem. Soc., *26*, 349-353 (1949).
4. Loeb, J. R., Morris, N. J., and Dollear, F. G., J. Am. Chem. Soc. (In press.)
5. Pominski, J., Molaison, L. J., Crovetto, A. J., Westbrook, R. D., D'Aquin, E. L., and Guilbeau, W. F., Oil Mill Gazetteer, *51*, (No. 12), 33-39 (1947).
6. O'Donnell, W. W., Food Ind., *19*, 763-768, 894, 896 (1947).
7. American Oil Chemists' Society, Official and Tentative Methods, 2nd ed., edited by V. C. Mehlenbacher, Chicago, rev. to 1948.
8. Jamieson, G. S., Vegetable Fats and Oils, Reinhold Publishing Company, New York, 1943, pp. 454-456.
9. Royce, H. D., and Kibler, M. C., Oil & Soap, *11*, 116-119 (1934).
10. Bailey, A. E., Cottonseed and Cottonseed Products, Interscience Publishers, Inc., New York, 1948, pp. 365-366.
11. Tyler, L. D., Food Ind., *20*, 1456-1459, 1618-1621 (1948).
12. Mattikow, M., Oil & Soap, *19*, 83-87 (1942).
13. National Cottonseed Products Association, Rules Governing Transactions Between Members, 1948-1949.
14. Bailey, A. E., and Feuge, R. O., Ind. Eng. Chem., *15*, 280-281 (1943).
15. Feuge, R. O., and Bailey, A. E., Oil & Soap, *21*, 78-84 (1944).

[Received July 15, 1949]