macaronis. Over the entire range of colors encountered, dominant wavelength was remarkably constant, and the purity and brightness values were sufficient to establish the macaroni colors observed. Of these two, brightness varied significantly only for samples which were brownish in color; otherwise purity alone would suffice to establish the color. Purity values for macaroni are very closely correlated with macaroni pigment values, and either will serve equally well as the color index for prediction tests. We have worked out the prediction test to yield macaroni purity values; but, except under special circumstances, we feel that macaroni pigment values are more readily understood and meaningful. It is also possible, with semolina, to use a single reflectance measurement in place of the semolina pigment determination, along with the semolina lipoxidase measurement, to predict either purity of macaroni or macaroni pigment.

Summary

It has been established that durum wheats contain lipoxidase and that the presence of this enzyme is responsible for the low correlation between the pigment content of semolina and the color of macaroni. By taking account of the lipoxidase factor and using a multiple regression equation, it is possible to predict macaroni pigment or percentage of purity of macaroni from measurement of semolina reflectance, semolina pigment, or wheat pigment.

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Ethanolamines and Other Amino- and Hydroxyl-Containing Compounds in the Refining of Rice Oil[1]

E. R. COUSINS, R. PRACHANKADEE,[2] and S. BHODHIPRASART,[2] Southern Regional Research Laboratory,[3] New Orleans, Louisiana

THE COMMERCIAL REFINING of crude rice oil with sodium hydroxide in the usual manner (3) generally results in losses that are much greater than would be expected from the characteristics of the oils.

While rice oils processed entirely under carefully controlled laboratory or pilot plant conditions have given refining losses similar to those of cottonseed oils with comparable free fatty acid content (6, 7, 13), the usual commercial losses are of such a magnitude as to make it very difficult, if not impossible, to refine rice oil economically.

Considerable effort has been expended in attempts to find a practical method of reducing these losses. The Japanese, in particular, have done a great amount of work on the refining of rice oil (8, 9, 10, 11, 12). In this country attempts have been made to refine rice oil, using special techniques (4, 13) and the many methods developed for decreasing the refining losses of other vegetable oils. However, as far as is known, no practical commercial method applicable to rice oil has been reported.

When normal refining procedures are employed, the foots formed from crude rice oil are unusual in their inability to cohere and settle out of the oil cleanly. The soapstock is usually composed of small individual grains. These grains settle very slowly, occlude considerable oil, and are almost as fluid as the oil itself. Without the use of special techniques for the separation of the soapstock, the refining loss on a comparatively good rice oil (content of free fatty acids, 5.5%) could be in excess of 50.0%. Centrifugation of the mixture or refining in solvents increases the yield of refined oil but still results in losses of about 25 to 30%. Similar reductions in refining loss may be obtained in the laboratory by simply filtering the mixture through a 100-mesh stainless steel screen (5).

The peculiar behavior of rice oil foots has been attributed to some unknown material in the crude oil that tends to emulsify the oil under the conditions of refining. Light non-settling foots are thus formed. In the past year the major objective of the research on rice oil in this laboratory has been to isolate and to identify this unknown material. The results of the initial phase of this work will be the subject of a forthcoming report.

Recently, in the preparation of liquid floor polishes containing high concentrations of rice wax in the solid portion, it was noted that the emulsions would invariably grain out as though no emulsifying agent were present whenever a triethanolamine soap was used as the emulsifying agent. The use of morpholine instead of triethanolamine, or carnauba wax instead of rice wax, resulted in stable emulsions. Apparently the triethanolamine was effectively neutralizing the emulsifying properties of the mixture.

Therefore an investigation of the effect of triethanolamine and related compounds in the refining of crude rice oil was undertaken. As a result of this investigation enough information has been gathered to provide the basis for future development of the problem. No attempt has been made to present a complete commercial process for the refining of rice oil.

Materials and Methods

Three samples of clarified crude rice oil and one of unclarified crude rice oil were obtained from commercial processors. The clarified oils, used in most of the work, were filtered through diatomaceous earth to insure uniformity of successive samples of each oil and to remove the last traces of solid wax. The unclarified rice oil was used as received. The clarified crude oil having a free fatty acid content of 5.5% was used to establish the preferred refining condi-

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[2] Department of Science, Ministry of Industry, Bangkok, Thailand.

[3] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

tions. Thereafter these conditions were tested using the other oils. Portions of two of the clarified oils were stored without filtering for one year at room temperature, and when they were used in the tests, their content of free fatty acids had increased from 5.5 to 6.6% and from 13.0 to 17.4%.

The ethanolamines and other additives used in the experiments were of technical grade and were obtained from commercial sources.

All cup refinings were based on the procedure for hydraulic cottonseed oil as prescribed in Official Method Ca 9a-52 of the American Oil Chemists' Society (1). In most of the cup refinings certain changes were made for the sake of reducing the time required and amount of materials needed for a test. Briefly, 100-g. samples of the crude oil were used, and the refinings were carried out in 250-ml. glass beakers. A 16° Bé. solution of sodium hydroxide was used in an amount sufficient to neutralize the free fatty acids and to provide an excess of 0.4% of solid sodium hydroxide. Agitation was provided by a stainless steel, paddle-type of stirrer. Stirrer speeds were regulated by a cone-driven mechanism to provide stirring speeds for the cold and hot mixtures substantially similar to those in the official method. Stirring times and temperatures were the same as those used in the official method. Refining losses were determined from the yield of refined oil shortly after the sample had cooled to room temperature (about 1 hr.). This modified procedure was capable of producing refining results which were reproducible and comparable to those obtained with the official method for hydraulic cottonseed oil. Any variations in the described procedure are mentioned in each case.

One series of cup refinings was carried out according to the official method for hydraulic cottonseed oil, changing only the amount and concentration of the sodium hydroxide solution employed.

The free fatty acid content and bleached color of the oils were determined by A.O.C.S. Official Methods Ca 5-40 and Cc 8a-52, respectively (1).

Experiments and Results

Addition of Triethanolamine. Various amounts of triethanolamine were added to the clarified oil containing 5.5% of free fatty acids, and the mixture was stirred rapidly for either 15 or 30 min. at different temperatures as shown in Table I. After rapid stirring for the specified time, each refining was completed as described in the general procedure. The minimum amount of triethanolamine used was calculated to give a quantity sufficient theoretically to neutralize the free fatty acids and to provide an excess of 0.4% on an oil basis. Water was added during the last minute of rapid stirring in an amount equal to that which would have been used to prepare a 16° Bé. solution of sodium hydroxide equivalent in amount to the triethanolamine employed. In one experiment, based on the patent literature (2), a large excess of triethanolamine was used, and no water was added.

TABLE I

Refining of Rice Oil with Triethanolamine[a]

Triethanolamine, %	Temp. during rapid stirring, °C.	Amount of rapid stirring, min.	Amount of water added,[b] %	Refining loss, %	Free fatty acids in refined oil, as oleic, %
3.4	27	15	10	12.4	2.0
3.4	27	30	10	11.1	2.2
3.4	45	30	10	11.2	2.4
3.4	90	30	10	7.4	2.6
6.0	27	30	17	23.8	1.7
9.0	27	30	30	18.5	1.2
33.0	27	30	0.0	17.4	0.62

[a] Clarified crude oil containing 5.5% of free fatty acids was refined in 100-g. batches.
[b] Water added in last minute of rapid stirring.

The results of the above refinings, given in Table I, indicate that triethanolamine was unable to reduce the free fatty acid content of the oil to a satisfactory level in spite of the fact that it is a weak base. Increasing the time of reaction from 15 to 30 min. actually caused a slight increase in the free fatty acid content of the refined oil; likewise increasing the temperature at which the refining was conducted caused a rise in the free fatty acid content. The amount of triethanolamine had to be in excess of about 10% to reduce the free fatty acids below 1%.

Addition of Triethanolamine and Sodium Hydroxide. The triethanolamine was mixed with the oil at room temperature for 15 min. before the solution of sodium hydroxide was added; then the refining was continued in the usual manner. The maximum amount of sodium hydroxide used was enough to neutralize the free fatty acids and to provide an excess of 0.4%; the amount of triethanolamine was the same in each test and was also sufficient theoretically to neutralize the free fatty acids and provide an excess of 0.4% on an oil basis.

TABLE II

Refining of Rice Oil with Triethanolamine and Sodium Hydroxide[a]

Amount of 16° Bé. lye, %	Refining loss, %	Free fatty acids in refined oil, as oleic, %
3.2	10.5	1.7
6.8	14.6	0.62
8.8	17.4	0.24
10.6	19.3	0.07
10.6[b]	44.1	......

[a] Clarified crude oil containing 5.5% of free fatty acids was refined in 100-g. batches with 3.4-g. of triethanolamine in addition to the 16° Bé. sodium hydroxide.
[b] Triethanolamine omitted in this test.

As indicated in Table II, only the maximum amount of sodium hydroxide reduced the residual free fatty acid content of the refined oil to an acceptable value. The triethanolamine remained effective in reducing the refining loss in spite of the large concentration of caustic. The loss with the maximum amount of caustic (0.4% excess) in the presence of the triethanolamine was very much lower than the normal refining loss with sodium hydroxide alone (44.1%).

In another group of experiments the amount of triethanolamine and the point in the refining process at which the triethanolamine was added were varied. Normally, various amounts of triethanolamine were added to the oil before the caustic. In two experiments however the procedure was changed; the triethanolamine was added with the caustic in one test and after the caustic in the other. Except for the point of addition and the length of time of mixing with the triethanolamine, the refinings were carried out as usual. The mixing times together with the results for this series of refinings are given in Table III.

In general, it may be concluded that the refining loss of this particular rice oil (normally 44%) may be reduced to below 20% by the addition of about 2.0 to 4.0% of triethanolamine. The triethanolamine

TABLE III

Effect of Triethanolamine as an Additive on the Refining Loss of Rice Oil [a]

Triethanolamine added	Triethanolamine, %	Duration of mixing after addition of triethanolamine, min.	Refining loss, %
Before caustic	0.5	15	58.1
	1.0	15	36.7
	1.5	15	23.8
	2.0	15	16.0
	3.0	15	20.7
	3.4	15	19.3
	1.0	1	34.5
	1.5	1	31.9
	2.0	1	23.4
	3.4	1	16.7
With caustic	3.4	....	19.3
After caustic	3.4	15	18.7

[a] Clarified crude oil containing 5.5% of free fatty acids was refined in 100-g. batches, using 16° Bé. sodium hydroxide in an amount sufficient to neutralize the free fatty acids and supply an excess of 0.4% of solid sodium hydroxide.

may be added to the oil before, with, or after the sodium hydroxide. The results obtained indicate that there may be an optimum amount of additive which will vary, at the very least, with the mixing time and the point at which the caustic is added. However no attempt was made to further develop this point.

Use of Other Additives. A group of other additives were tested under comparable refining conditions. The additives were stirred into the oil first for 15 min. The oil was then refined as usual with 16° Bé. caustic. The results of the experiments are given in Table IV.

Significant reductions in refining loss were obtained with all of the additives except triethylamine. Monoethanolamine proved to be the most effective additive; however sucrose or blackstrap molasses, being less expensive, would probably be more attractive for a commercial process.

TABLE IV

Effect of the Addition of Several Organic Compounds and Products on the Refining Loss of Rice Oil [a]

Additive [b]	Amount added, %	Refining loss, %
None	....	44.1
Triethanolamine	3.4	20.3
Monoethanolamine	1.8	17.4
Tetraethanol ammonium hydroxide	5.3	17.5
Ethylene diamine	1.8	18.7
Ethylamine	1.5	20.4
Ethylene glycol	1.9	20.3
Ethyl alcohol	1.5 3.0	46.0 24.0
Triethylamine	2.8	53.2
Sucrose	1.5	30.0
Blackstrap molasses	2.5	23.3

[a] Clarified crude oil containing 5.5% of free fatty acids was refined in 100-g. batches, using 16° Bé. sodium hydroxide in an amount sufficient to neutralize the free fatty acids and provide an excess of 0.4% of solid sodium hydroxide.

[b] Additives were mixed with the oil for 15 min. before refining.

The results of the experiments as given in Table IV also indicate that either the NH_2 or OH group or a combination of these groups is capable of reducing the refining loss. The amines apparently do not exert their influence through the formation of a salt because compounds without the amine group, like ethylene glycol, are effective while triethylamine is not.

Comparative Refinings of Three Crude Oils. Three clarified crude rice oils were refined with and without monoethanolamine. A 0.4% excess of both the monoethanolamine and 16° Bé. sodium hydroxide was used. After mixing the monoethanolamine and the crude oil for 1 min., the refining procedure for hydraulic cottonseed oil as given in the Official and Tentative Methods of the A.O.C.S. was followed in detail. The marked improvement in the refining losses with additive refining and the similarity of the refined oils produced by both refining procedures is evident from the results listed in Table V.

Application to Continuous Refining. The continuous refining of rice oils containing 5 to 7% of free fatty acids normally results in a loss of 25 to 30%. To determine if the use of additives would result in a greater yield of oil on refining by the continuous method, the unclarified rice oil (containing wax and having a free fatty acid content of 4.5%) was refined in a sludge discharge centrifuge. Two batches of this oil were refined in exactly the same manner except that 2.5% of blackstrap molasses in 5% water (all on an oil basis) was added to one batch a minute before the addition of the caustic. Normal refining resulted in a loss of 31.6% while refining with the additive resulted in a loss of 16.8%.

TABLE V

Effect of the Addition of Monoethanolamine on the Refining Loss of Three Clarified Crude Rice Oils [a]

Sample	A		B		C	
Free fatty acids in crude oil, as oleic, %	5.7		6.6		17.4	
	Test	Control	Test	Control	Test	Control
Monoethanolamine,[b]%	1.6	....	1.8	....	4.1	....
Refining loss, %	21.5	50.9	17.2	44.1	41.5	61.6
Refined oil, free fatty acids,%	0.026	0.042	0.037	0.032	0.032	0.045
Bleached color, Lovibond, yellow/red	70/5.3	70/6.1	35/3.2	35/2.5	70/11.3	70/12.0

[a] Procedure employed was that specified for hydraulic cottonseed oil in A.O.C.S. Method Ca 9a-52 except that an additive was used and the 16° Bé. sodium hydroxide used was sufficient to neutralize the free fatty acids and supply an excess of 0.4% of solid sodium hydroxide.

[b] Additive mixed with the crude oil for 1 min. before the addition of the lye.

Application to Cottonseed Oil. Processors are familiar with the fact that the refining of certain "off-grade" crude cottonseed oils results in soft soapstocks and unusually high losses. One of these cottonseed oils with a free fatty acid content of 2.0% and a refining loss of 23.9% by standard A.O.C.S. procedure was refined, using monoethanolamine as the additive. The ethanolamine (1.5%) was added 1 min. before starting the normal refining procedure. Use of the additive reduced the loss to 10.1%, indicating that the additives are effective with at least some crude cottonseed oils.

However the additives are not able to reduce further the refining loss of a normal crude cottonseed oil; in fact, the presence of 1.5% by weight of monoethanolamine adversely affects the refining loss of such an oil. For example, a crude cottonseed oil having a free fatty acid content of 0.6% was refined with and without the additive, resulting in losses of 5.5% and 3.6%, respectively.

Summary

In the alkali-refining of rice oil by the usual procedure employed for cottonseed and similar oils excessive losses occur. A rice oil containing about 5% of free fatty acids may refine with a loss of over 40% by the cup method.

A series of experiments has been performed which shows that the adding of certain organic compounds to the crude oil just before carrying out the regular refining procedure greatly reduces the refining losses. The technique was effective in both batch and con-

tinuous processes. Depending on the refining process used, reductions in the refining loss of 32 to 55% have been obtained.

The organic compounds used as additives contained NH_2 and OH groups. Sucrose or blackstrap molasses appears to be the most practical material to use. However ethanolamines and various glycols and alcohols may also be employed.

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The Recovery of Phosphatides from Direct Extracted Cottonseed and Reincorporation into the Meal[1]

W. C. WHITTECAR, Plains Cooperative Oil Mill, Lubbock, Texas

THE PLAINS COOPERATIVE OIL MILL in 1952 purchased a French continuous solvent-extraction plant with the plan in mind of direct extraction of cottonseed. On April 6 the first trial run was made on prepress cake from eight French expellers. This operation was continued for 10 days. Then operations were changed to direct extraction without cooking, giving us a highly soluble protein meal. Although considerable trouble was encountered in processing during the first six months of operation, this process is in operation at the present time.

We, like other solvent operators, have experienced considerable resistance to acceptance of solvent meal by feeders and feed manufacturers. Their complaints about solvent meals were that the meals contained less fat, were dusty, and would not mix well (that is, would separate from other ingredients and grains in a balanced ration); livestock, in general, would not eat them because of unpalatability. Pellets made from straight solvent meal have never been satisfactory unless some other additive was used to soften the pellets.

A year ago we were seriously considering the installing of a complete refinery, using soap stock for the improvement of our meal and products. We are cottonseed crushers, and this would have put us into a new field about which we knew nothing. We still prefer to sell our crude cottonseed oil to the people who make refining their business.

We sincerely believe that the process we now have is not only going to help meal problems in solvent operations, but we are going to be able to deliver to refineries a much improved crude oil.

After considerable investigation the final decision was to water-wash and degum our crude cottonseed oil, thus producing a commercial cottonseed lecithin. This product would not only solve the problems regarding solvent meal, which I have mentioned before, but would give us what we believe to be a feed ingredient high in nutritive value to reincorporate into our meal. This process has proven to be very satisfactory from the first day of operation, both on meal and pellets. It has also made possible an increase in tonnage through all equipment connected with the operations. It has enabled us to move the product into districts where screw press and hydraulic meals have been the dominating products. The new product is hard to distinguish from either screw press or hydraulic meals in texture, color, fat content, and mixing qualities.

BUT IN doing these things a problem developed in regard to the oil. A very fine oil was produced, low in refining loss, low in color, and low in bleach; but its color and acidity increased in transit to delivery points.

In carrying out the degumming operations, the following method is used:

Crude cottonseed oil at normal temperature (80° to 90°F.) is pumped into a surge tank in the degumming plant. This oil is then pumped into a base vertical, high-speed mixer, where 2% warm water is injected. The mixture of water and oil flows up through the mixer forming a semi-emulsion. Upon leaving the mixer, the oil goes to a thermostatically controlled heating coil where temperature is raised to 130° to 140°F. It is then discharged into two VO 194 DeLaval Hermetic Sealed Centrifuges, turning 7,500 r.p.m. and operating under a back pressure of 60 p.s.i. Here the phosphatides are separated from the crude oil. The gums as they emerge from the centrifuge contain 35% to 45% water and from 85% to 95% acetone-insolubles.

The gums are pumped immediately into the second ring of the desolventizer toaster, where the hexane, which is present, is used to distribute the gums uniformly in the flakes. The vaporization of hexane from the flakes results in a complete adsorption of gums into the flakes. As stated previously, when the gums are incorporated into the flakes, a product results which increases the efficiency of the equipment and increases the speed of pelleting 125%. It also cuts down the wear on dies.

After the gums are separated from the oil, the oil leaves the centrifuge with .4% to .8% moisture. It goes into a heating coil where the temperature is increased to 150° to 160°F. before going to a vacuum drier where the moisture is removed. The oil is then taken from the drier and immediately cooled to 85° to 90°F. prior to storage.

As indicated before, considerable trouble was experienced in drying the oil and in maintaining color

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