Miscella Refining Test Method for the Determination of Cottonseed Oil Color

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ABSTRACT: Most of the cottonseed oil mills in the United States have already converted to expander solvent extraction and miscella refining. This practice permits mills to produce and market a consistently light-colored, prime bleachable summer yellow cottonseed oil at reduced cost and refining loss. A laboratory-scale miscella refining test was developed to assess the oil quality in terms of its color. The test involves the addition of 3 parts oleic acid per 100 parts of crude oil in the miscella followed by refining with 2.5 parts NaOH when crude oil contains less than 4.5% free fatty acid (FFA). When crude oil contains FFA between 4.5 and 7.5%, no oleic acid is added prior to refining with 2.5 parts NaOH. When crude oil contains FFA higher than 7.5%, no oleic acid is added and the caustic addition table in American Oil Chemists' Society Method Ca 9a-52 is followed. The test was conducted at room temperature and gave reproducible colors comparable to commercially refined oils.
JAOCS 73, 815–817 (1996).

KEY WORDS: Cottonseed oil, miscella, miscella refining, oleic acid, PBSY, refined color.

Two major changes in cottonseed oil processing during the past thirty years have significantly improved productivity and oil quality. Introduction of the expander, a low shear extruder, improved the throughput of existing facilities by more than 20% with little retrofit (1). At the same time, the continuous demand for lighter colored oil has motivated cottonseed processors to incorporate miscella refining into the normal oil extraction process. This has produced once-refined oil that easily meets the quality of prime bleachable summer yellow (PBSY) and has reduced refining loss (2–7). These changes overall reduced the cost of cottonseed products, while delivering a consistent-quality oil.

Although these changes have taken place in the cottonseed processing, analytical methods for quality evaluation of oilseed and oil products have remained largely unchanged. Most standards used in the trading rules of the industry are measured by methods developed in the 1950s and are outlined in the American Oil Chemists' Society (AOCS) Methods handbook (8). The refining procedure described in AOCS Method Ca 9e-52 (8) is different from the current miscella refining procedure and often results in much darker oils than plant-refined oils. This is shown in Table 1, where the colors of plant miscella-refined oil samples are compared to refined crude oil samples obtained at the same time but which were caustic-refined in a commercial laboratory. The official test method also requires a minimum of 500 g of crude oil or preferably 1.5 kg, is excessively time-consuming, and requires tedious heating and cooling cycles. It also needs specialized equipment and specific stirring speeds, which are difficult to reproduce with alternate equipment. The purpose of this research was to develop a laboratory-scale miscella refining test for cottonseed oil with less than 500 g crude oil and to achieve a refined-oil color similar to that of the PBSY produced by miscella-refining in modern cottonseed oil mills.

TABLE 1
AOCS Red Color of Plant Refined Oils (prime bleachable summer yellow) and Caustic Refined Oils

	Refined	
Sample code	Plant miscella	Caustic[a]
1993 Processing season		
GMS713	3.9	5.6
GMS714	4.0	4.6
1994 Processing season		
MLA312	4.0	8.6
MLA314	4.0	9.0

[a] Refined by a commercial laboratory according to AOCS Method Ca 9e-52 (Ref. 8). Oils supplied by Yazoo Valley Oil Mill (Greenwood, MS).

EXPERIMENTAL PROCEDURES

Materials. Crude and once-refined PBSY cottonseed oils were supplied by Yazoo Valley Oil Mill (Greenwood, MS) during 1993 and 1994. Refined colors of these oils are given in Table 1. The crude oil was produced by an expander solvent mill and contained 1% free fatty acid (FFA), 0.476% gossypol, and 700 ppm phosphorus. Sodium hydroxide solution, 50% by weight, diatomaceous earth, and sodium oleate were obtained from J.T. Baker, Inc. (Phillipsburg, NJ). Purified oleic acid was obtained from Fisher Scientific Company (Fairlawn, NJ). A high-shear disperser, Ultra-Turrax T-25, made by James & Kunkel GMBH & Co. (Staufen, Germany) was used to homogenize the caustic solution with the crude cottonseed oil—commercial hexane miscella. Commercial hexane was supplied by Phillips Petroleum Company (Bartlesville, OK).

Methods. Caustic refining of plant-produced crude oils was performed by a commercial laboratory according to AOCS

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Method Ca 9a-52 (8), and refined color was read according to AOCS Method Cc 13b-45 (8) or measured with a Colourscan (Tintometer Ltd., Salisbury, United Kingdom) automated colorimeter (9). Color of oil samples refined in our laboratory was determined by Colourscan in a 133.4-mm cell and reported as AOCS red scale. A miscella concentration of 60% was used throughout this study. The caustic level was calculated from the tables given in AOCS Method Ca 9a-52 (8). Concentration of NaOH at 13% by weight was used in this study. Soapstock was separated by centrifugation with a Dynac II centrifuge (Clay Adams, Parsippany, NJ) at 2000 rpm for 15 min; the refined miscella was decanted and filtered through Whatman No. 4 filter paper (Maidstone, England). Refined oil was obtained by desolventizing the miscella in a rotary evaporator at 55°C and 125 mm Hg (25 inches Hg) vacuum. Color of refined oil was measured with the Colourscan as described above.

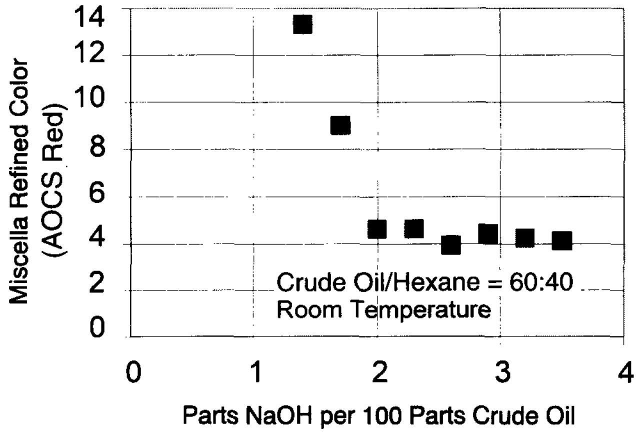

FIG. 1. Effect of caustic levels on miscella-refined oil color; AOCS, American Oil Chemists' Society.

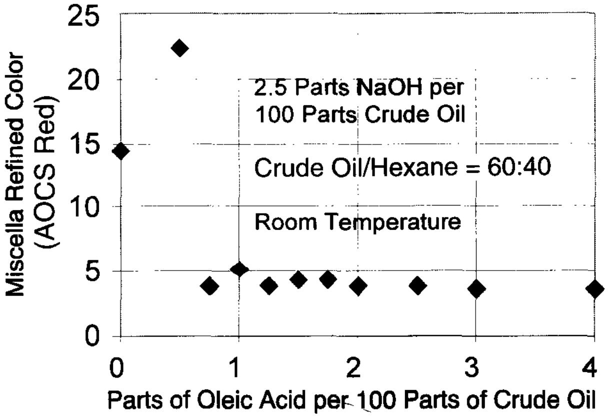

FIG. 2. Effect of oleic acid level in miscella on refined oil color with 2.5 parts NaOH for refining. See Figure 1 for abbreviation.

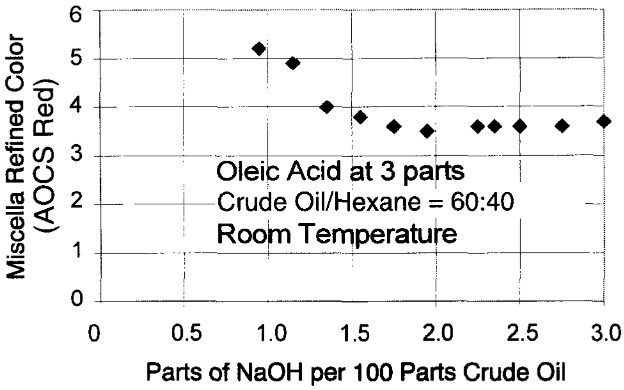

FIG. 3. Effect of caustic levels on refined oil color with three parts of oleic acid added to the miscella prior to refining. See Figure 1 for abbreviation.

RESULTS AND DISCUSSION

A simple miscella refining experiment was conducted according to the conditions described in the Experimental Procedures section to evaluate miscella refined oil color. All work was performed at room temperature without heating and cooling steps. Because the crude cottonseed oil used for this experiment contained 1% FFA, one part NaOH per 100 parts of oil was added to the 60% miscella [(Table 5 of AOCS Method Ca 9a-52)] (8). Refined oils from six repeated trials were dark with AOCS red colors of 41.6, 36.0, 40.0, 21.2, 26.8, and 29.2, respectively. This simple experimental procedure apparently showed little reproducibility.

Effect of increased dosage of NaOH. In the next set of experiments, we varied the level of caustic addition but kept the same refining procedure described above. The color of the refined oil, displayed in Figure 1, showed drastic improvement when the caustic level was increased to more than 2 parts per 100 parts of crude oil. This is much higher than the recommended caustic level from AOCS Method Ca 9a-52 for a crude oil containing 1% FFA (8).

Effect of added oleic acid at constant level of NaOH. In an effort to further improve the refined color and reproducibility of miscella refining, various amounts of oleic acid were blended with the miscella before refining with 2.5 parts NaOH. Results are shown in Figure 2. At higher than 2 parts oleic acid per 100 parts crude oil, the maximum color removal is achieved, and a more consistent miscella-refining color is observed. When 3 parts of oleic acid per 100 parts crude oil were added to the miscella, addition of caustic at the rate of more than 1.75 parts achieved the lightest refined color (Fig. 3).

Holding time for the homogenized miscella. Figure 4 demonstrates the refined color obtained at different coagulation holding times after homogenization of 2.5 parts caustic with miscella containing 3.5 parts added oleic acid. It is apparent that a steady miscella-refined oil color was already reached after holding the homogenized miscella for an hour. But with longer than 20 h holding time, there is still a slight improvement in color.

Proposed miscella refining test. Based on the experimental results, the following lab-scale miscella refining procedure is

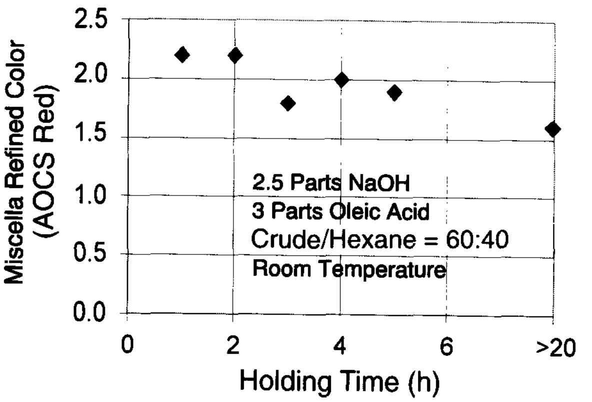

FIG. 4. Effect of holding time of refined miscella on refined color. See Figure 1 for abbreviation.

proposed for crude cottonseed oil: (i) In a 500-mL wide-mouth Erlenmeyer flask, adjust miscella concentration to 60% (120 g crude cottonseed oil and 80 g hexane); (ii) when FFA level of the crude oil is less than 4.5%, add 3 parts or 3.6 g oleic acid (when FFA is higher than 4.5%, no oleic acid is needed); (iii) add enough water to the miscella to make final NaOH 13% by weight (add 17 g water to the miscella); (iv) add 2.5 parts NaOH per 100 parts crude oil (add 6.0 g of 50% wt NaOH) [When FFA is higher than 7.5%, follow caustic table in Ca 9a-52 (Ref. 8).]; (v) homogenize with Ultra-Turrax T-25 high shear disperser at 24,000 rpm for 2 min; (vi) add 3 g diatomaceous earth and mix vigorously; (vii) allow a minimum of 3 h coagulation time; (viii) compact soapstock by centrifuging at 1500 rpm for 15 min; then filter miscella through a Whatman No. 4 filter paper; (ix) desolventize refined and filtered miscella at 55°C and 125 mm Hg (25 in Hg) vacuum.

Repeatability of the proposed miscella refining method. Replicate miscella refining of several plant-produced oils was carried out according to the proposed experimental procedure. Results in Table 2 showed a standard deviation of less than 4% of the mean values of AOCS Red for three types of crude oils derived from commercial expeller, prepress-solvent, and expander–solvent processes. Colors of miscella-refined expeller and prepress-solvent processed oils in our laboratory by the proposed procedure are much darker than those from the expander–solvent processed oil, due to long room-temperature storage conditions. The nature of this color fixation phenomenon will be further investigated.

Addition of various amounts of sodium oleate to the caustic aqueous phase prior to homogenization did not yield the same results as adding oleic acid to miscella before refining. It is crucial that sufficient soap is formed during miscella refining for removal of the natural impurities, especially pigments and color-forming components in the crude cottonseed oil derived from the cottonseed crushing and extraction process. This proposed miscella refining procedure offers researchers a tool to assess oil quality in terms of color by refining procedures similar to those used in cottonseed processing plants.

TABLE 2
AOCS Red Color of Replicate Miscella Refining Tests of Three Different Types of Crude Cottonseed Oils[a]

Sample	1	2	3	Mean	SD
LMS113 (expander–solvent)	3.5	3.6	3.6	3.6	0.1
CCA630 (prepress solvent)	10.2	10.0	9.8	10.0	0.2
RTX614 (expeller)	7.5	7.6	8.0	7.7	0.3

[a] Oil samples were supplied by the member mills of the National Cottonseed Products Association (Memphis, TN).

Cottonseed oil is traded on its bleachable color for PBSY and its FFA content and refining loss for crude (7). Miscella-refined oil will be traded as PBSY when its bleached color is less than 2.5 AOCS Red (7). To improve quality control in the ever-changing cottonseed processing technology, researchers need a simple and reproducible refining method to examine the quality of oil at the point of refining, so that the refining process can be tracked or modified. Further, the conditions of seed preparation are believed to have a strong causative effect on final oil quality, which may be assessed by the proposed miscella refining test. It is also highly desirable to develop a refining test that can assess both refined color and refining loss under normal miscella-refining conditions and that will also predict the bleachability of oil. This will be investigated.

ACKNOWLEDGMENTS

The authors thank members of NCPA and Cotton Incorporated for their technical advice and financial support.

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[Received November 8, 1995; accepted March 20, 1996]