Relationships Between Moisture Contents of Cottonseed Flakes and Water in Miscellas from Extractions with Acetone-Cyclohexane Azeotropes

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Abstract

A method for determining the composition of acetone, hexane and water mixtures was adapted for use with acetone, cyclohexane and water mixtures.

Techniques for drying cottonseed flakes to different moisture contents for extraction with acetone-cyclohexane azeotropes were devised. Tests for possible gossypol binding occurring during the drying operation were made.

Bench scale extractions yielded data which show the water resulting in miscellas when extracting cottonseed flakes at various moisture levels.

It is envisioned that in a commercial process utilizing an acetone-cyclohexane-water mixture to produce cottonseed protein products for food uses, the water in the extracting mixture would be stablized at a level somewhere between the 0 and 3% by wt water levels of the two azeotropes used in these studies.

Efforts are currently being devoted to defining the optimum practical water level that could be easily attained in commercial usage. Additional products evaluations will also be made.

Introduction

UNLIKE SOLVENT EXTRACTION operations involving the use of a single solvent to remove oil or gossypol from raw cottonseed flakes, extractions in which a solvent mixture is used may require more precise controls in recovering and preparing the mixed solvents for reuse. Especially is this true if one or more of the solvents comprising the mixture is water miscible.

Water may then either be removed from the flakes by the extracting solvent or from the solvent by the flakes depending on the relative percentages of moisture contained in each.

By knowing the relationship between moisture contents in flakes extracted and the water resulting in miscellas, optimum extraction conditions can be sought by adjusting the flakes moisture for a given solvent mixture and ratio of solvent to flakes.

It is imperative that a simple and sufficiently accurate method of determining the composition of solvent mixtures recovered from miscellas be available.

King and Frampton (1) have described a method for analyzing mixtures of commercial hexane, acetone, and water. The method was tested and adapted for application to solvent mixtures recovered from extractions with acetone-cyclohexane azeotropes in the investigations reported here.

Acetone and cyclohexane form a binary azeotrope which is 67.3% acetone and 32.7% cyclohexane by weight and boils at a lower temperature (53.1C) than either acetone or cyclohexane. The addition of water to a mixture containing acetone and cyclohexane has the effect upon distillation of producing a ternary azeotrope of acetone, cyclohexane and water in which the cyclohexane concentration is raised and the acetone concentration is lowered as indicated by the data which follow (2):

Distillation of Acetone-Cyclohexane Mixtures With and Without Water in Mixtures

Acetone wt %	Cyclohexane wt %	Water wt %	Boiling Point °C
67.3	42.7	0	53.1 ± 0.5
55.5	41.5	3.0	52.2 ± 0.5

In mixtures containing less than 3% water the concentration of acetone and cyclohexane in the distillate will vary accordingly, i.e, less cyclohexane, more acetone.

The desirability of extracting uncooked cottonseed flakes with solvent mixtures capable of removing the gossypol and oil simultaneously and yielding a high quality protein product suitable for food uses by nonruminants, including humans, has been adequately stated by others (3,4).

Experimental extractions at the Cottonseed Products Research Laboratory with the acetone-cyclohexane mixtures described here have yielded cottonseed meals, desirably low in both gossypol and oil and high in protein quality as indicated by nitrogen solubility tests.

Experimental

Water Determination

Acetone and cyclohexane were mixed in the proportions occurring in the binary azeotrope. Nine samples were prepared by adding water in quantities varying from 0.5–4.0% by weight. Twenty five milliliter aliquots of each sample were transferred by pipette to 100 ml ASTM oil tubes. Commercial hexane was added until filled to the 100 ml mark. The tubes were stoppered, shaken throughly, and centrifuged for 5 min at 1000 rpm in an International Size 2 Centrifuge.

The heavier water layer separating at the base was measured with tube graduations.

The tube was calibrated from its lower tip in 0.05 ml subdivisions for the first ml; from 1 to 3 ml in 0.10 ml and from 3 to 6 ml in 0.20 ml. Four determinations were made on each sample and the readings averaged. Average tube readings multiplied by

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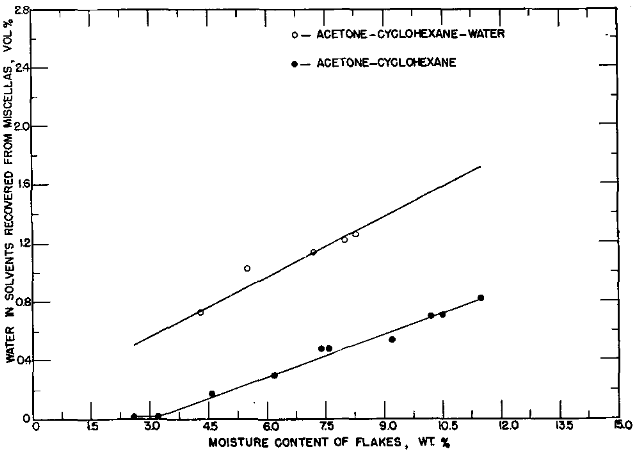

FIG. 1. Effect of moisture in flakes extracted upon water occurring in miscellas.

4 were plotted against the vol % of water known to be present in the mixture. A straight line graph of the form Y = MX + C, where M = slope and C = a constant determined by the point of intercept on the Y axis, was obtained.

An equation was derived from the graph for use in converting tube readings on unknown samples to vol % of water as follows:

Vol % of H_2O = 4 (0.483T) + 0.54

Where: T is the tube reading in ml; 0.483 is the slope; 0.54 is the intercept of the Y axis; 4 is multiplier to give % directly.

Cyclohexane Determination

Ten milliliter aliquots of acetone-cyclohexane-water mixtures of known composition were pipetted into 9 g. Babcock cream test bottles with calibrations along the necks from 0–50% in 0.5% divisions.

Each bottle was filled to a point below the uppermost graduation with distilled water, stoppered and its contents shaken throughly. Centrifugation followed for 5 min at 1000 rpm.

The resulting supernatant layer of cyclohexane, held entirely within the calibrated bottleneck was measured directly by reading the vol % spanned by the menisci.

Acetone Determination

The volume per cent of acetone was taken as 100 minus the combined volume per cent of water and cyclohexane.

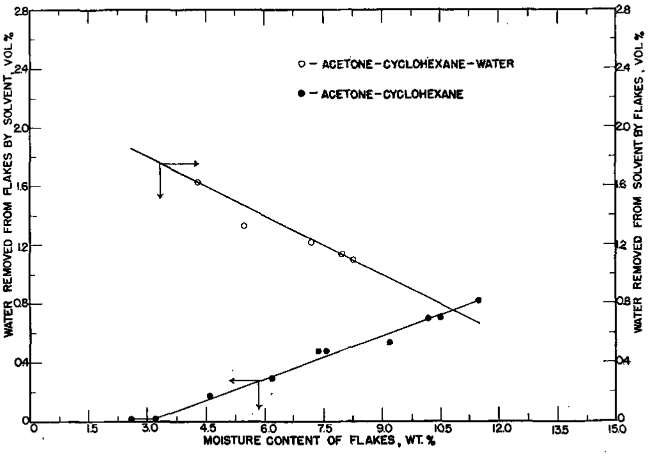

FIG. 2. Pattern of water movement between solvent mixtures and flakes extracted for different moisture levels in flakes.

Commercial grade 98% cyclohexane, commercial grade acetone and distilled water were used to prepare the mixtures studied.

Drying Cottonseed Flakes for Extraction

Cottonseed meats were prepared for extraction by moistening to 11.5% and allowing a 20 min setting period for the moisture to penetrate. Meats were flaked with smooth, one-pair high flaking rolls, 15 in. in diameter and 24 in. long. Flake thickness was 0.010 in.

Different moisture contents in flakes were achieved by drying in a forced draft circulation oven adjusted to a constant temperature of 180F. Three-pound quantities of flakes placed in a perforated metal tray lined with No. 16 mesh screen wire were representatively sampled after sufficient drying time to give the moisture sought. Depth of flakes in bed was 2 in.

Dried flakes were sealed in air tight containers upon removal from the oven and analyzed for moisture immediately prior to extraction.

Extraction Apparatus and Techniques

Bench scale extractions with the acetone-cyclohexane binary were made in duplicate using a percolation type extractor similar to a Butt type extractor. Fifty-gram samples of flakes were held in cylindrical wire baskets constructed of No. 16 mesh screen wire. Pads of glass wool were placed beneath the sample holder and above the flakes.

Miscella drained into a round bottom flask resting on a steam bath. Vaporized solvent traveled through a side arm to a condenser over the sample, where it liquified and continously returned to percolate through the flakes for a 2 hr period. The solvent to flakes ratio was 6:1 by weight.

A roll of No. 16 mesh wire, 4 in. long and 0.4 in. in diameter positioned in the center of the sample holder permitted a more uniform solvent permeation of the flakes.

In extractions with the acetone-cyclohexane-water ternary, an extraction procedure designed to simulate countercurrent type extractions was employed. Extractions were made in the Butt type extractors used with the binary mixtures but without provision for vaporizing and recycling solvent from the miscella.

Four 50 g samples dried to test moisture were extracted ahead of the test sample to provide suitable miscellas of three different oil concentrations. The miscellas were then used to extract the test sample followed by a 2:1 solvent to flakes ratio by weight of fresh mixture. The total solvent to flakes ratio was 6:1 by weight.

Single extractions were made at each moisture level. Solvent passed through the sample resting directly on a glass wool pad. A stop cock regulated the rate of miscella drainage. No heat was applied at any point.

A sample of the starting ternary mixture was distilled along with the miscellas from the test extractions and the recovery analyzed to establish a point of reference for gauging changes in water content of the mixture.

Results and Discussion

In determining water, no tube reading was obtained until water in the sample exceeded 0.54 vol %. To measure water present in lesser amounts 1% of water by volume was added to the sample before testing and then subtracted from the results measured.

The accuracy of the method for water was such that in the analyses of 6 known mixtures varying in water from 1 to 3.5 vol % the average deviation of the measured values from the expected values was 0.047 vol %. The maximum difference was 0.1 vol %.

The measured cyclohexane in the same 6 samples differed from the actual by an average of 0.22 vol %. The maximum deviation was 0.3 vol % for a single reading. All measured values were higher than expected values.

Two series of drying tests were made to ascertain whether any gossypol binding would occur in the oven during the drying operation.

Samples containing 11.7% moisture were placed in the oven in wire baskets for periods of 1 hr with the oven set at 180, 190, 200, 210 and 220F. An unheated sample was also analyzed for free and total gossypol.

None of the dried samples were found to contain more bound gossypol than the undried flakes.

In a second test the oven temperature was held constant at 180F and the drying period varied from 60 to 210 min. Here again, analyses of the dried flakes revealed no evidence of lowered free gossypol as a result of drying under these conditions.

Relationships between flakes moistures and water in miscellas when extracting with the binary and ternary azeotropes are given in Figure 1.

Patterns of water movement between the flakes and the solvent mixtures are shown in Figure 2.

Flakes were dried to a moisture content of 3% before the binary ceased to remove water from the flakes.

A point at which the flakes ceased to remove water from the ternary was not established.

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The Equivalence Test of the Earth to Become Known as Our 1964 Standard Earth

Composite samples were taken during the manufacturing of the 18 tons (450—80 lb bags) of earth that was manufactured by Bennett-Clark in June 1964. This sample was mixed, divided and portions sent to each of the 14 members of the committee. Tests were made on this earth to determine the exact percentage to be used. Each laboratory used its own refined oil, thus giving us a wider range of oils. Seven laboratories used soybean oil, and the other seven used cottonseed oil. Each laboratory made 4 bleaches in duplicate on the same oil. These bleaches were:

1. 4.67% new earth on c/s or 3.0% on s/b.
2. 5.67% new earth on c/s or 3.5% on s/b.
3. 4.17% new earth on c/s or 2.5% on s/b.
4. Standard percentage of the current standard (1954) earth (4.67% for cottonseed and 3.0% for soybean).

The above bleaching tests were made in accordance with the Official AOCS Method. Mr. Coleman and Mr. Clause were asked to run a spectro curve on tests No. 1 and No. 4.

A second experiment was made to determine if there was a significant difference between the bags of earth. This test was made in accordance with the procedure given by Mr. David McLean of the AOCS Statistical Committee. An outline of the procedure is as follows: The 450 bags were divided into six sections of 75 bags each. Three bags were sampled from each of the 75 bag lots. The number of the bag to be sampled from each lot was determined by placing slips of paper numbered from 1 to 75 and drawing three numbers at random. The same procedure was used for the other 5—75 bag lots. The sample from each bag was mixed well and divided

TABLE I

Bleaching Tests with Cottonseed Oil
Type and Percentage of Earth Used

Laboratory	AOCS Standard Earth 4.67%	June 1964 Earth 4.67%	June 1964 Earth 5.17%	June 1964 Earth 4.17%
Paymaster	2.8 2.9	2.8 2.8	2.8 (5.27%) 2.7 (5.27%)	2.8 (4.27%) 2.8 (4.27%)
Milwhite	2.6 2.6	2.8 2.8	2.6 2.6	2.9 2.9
Anderson, Clayton	2.8 2.9	2.7 2.7	2.6 2.5	2.8 2.8
Barrow-Agee	2.8 2.8	2.8 2.8	2.7 2.7	3.0 3.0
Filtrol	6.6 6.5	6.2 6.3	5.9 6.0	6.5 6.6
Paymaster	5.2	5.2 (A very dark oil)		
Hahn	3.1 3.1	3.1 3.1	2.9 3.0	3.3 3.3

TABLE II

Bleaching Tests with Soybean Oil
Type and Percentage of Earth Used

Laboratory	AOCS Standard Earth 3.0%	June 1964 Earth 3.0%	June 1964 Earth 3.5%	June 1964 Earth 2.5%
Votator	1.2 1.2	1.2 1.3	1.0 1.1	1.3 1.4
A.D.M.	1.7 1.6	1.6 1.7	1.3 1.2	1.9 2.0
A. E. Staley	1.6 1.6	1.6 1.6	1.4 1.4	1.8 1.8
Central Soya	1.4 1.4	1.4 1.4	1.3 1.3	1.6 1.6
Bennett-Clark	1.6 1.6	1.6 (9 times)		
Procter & Gamble	2.1 2.1	2.0 2.0	1.8 1.8	2.2 2.2
Hahn	2.5 2.5	2.5 2.5	2.3 2.4	2.6 2.7