An Aqueous Ethanol Extraction Process for Cottonseed Oil[1]

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ABSTRACT

A bench-top process for the extraction of cottonseed flakes with aqueous ethanol has been developed. The process consists of cottonseed meat flaking, drying and extraction with boiling, aqueous ethanol (95% by volume) at atmospheric pressure. The resulting miscella is chilled, producing free oil, emulsified oil and mucilaginous gum. The heterogeneous solution is processed through a phase separator where free and emulsified oil and gum are separated from oil-lean miscella. The oil and gum phases are treated with caustic soda and centrifuged to produce semirefined oil containing about 4% volatiles. The miscella phase, containing about 3.3% lipid-like material and 1% petroleum ether insolubles, is reheated and recycled to the extractor. After the marc is pressed foots are added, and it is desolventized to produce a meal having a residual oil content less than 1%. Although not yet optimized, the process shows potential for scaleup to pilot plant processing and adaptability to current oil mill solvent operations.

INTRODUCTION

Twenty years ago, AOCS President Dr. Ernest MacGee, in a talk to an International Superintendents' Association Convention, predicted that shortages of hexane could become evident before long (1). In the spring of 1980, his prediction came true (2). Although we now have a glut of petroleum products on the market, we are consuming them faster than we are finding new sources, and it is inevitable that they eventually will be exhausted. Although we cannot reliably predict when that time will come, we do know that then it will be too late to start looking for an alternative for hexane as a vegetable oil extractant. It was with this thought in mind that we initiated a project whose main objective was to find a biorenewable solvent alternative to hexane. Although hexane is flammable and explosive and the government has set limits for air emissions and human contact, it still remains the solvent of choice for vegetable oil extraction in the U.S. An additional objective of our research is the development of a simplified extraction process adaptable to present extraction processing equipment with a minimum of modification.

Based on these two considerations and an extensive review of the existing literature (3), we selected aqueous ethanol, in particular the 95% by volume azeotrope, as the alternative to hexane. Ethanol is obtainable from biorenewable resources and is one of four vegetable oil solvents (water, ethanol, butane and propane) that are generally recognized as safe, as stated in a private communication from the Food and Drug Administration. Ethanol at or near its boiling point is a good solvent for vegetable oils, but at ambient temperatures and at decreasing alcohol concentrations, its oil solubility significantly diminishes (4). The Japanese in Manchuria in the 1930's capitalized on this solubility characteristic and commercially extracted soybeans with 95% ethanol (4-6). However, their process included an energy intensive step—the evaporation and recovery of non-oil solubles from miscella at the conclusion of each cell extraction. Beckel and co-workers later refined the process, reducing energy requirements by 25% over a comparable soybean-hexane process (7). Rao and Arnold adapted Beckel's process to cottonseed using 95% ethanol in pilot plant extraction studies, but they ignored the problem of precipitated gums and more importantly could not reduce residual oils in the marc below an uneconomical 1.54% (8).

Karnofsky recently has developed a unique but somewhat complicated four-step process using 90% ethanol first to extract aflatoxin and/or gossypol, fatty acids and non-oil lipids and then 95% ethanol to extract oil (9,10). By extracting the oil and gums separately he obtained low residual lipids. Although he avoided the precipitated gum problem, the dilute miscella produced must be both evaporated and rectified in order to recover concentrated ethanol.

MATERIALS AND METHODS

Industrial grade 190 proof ethanol (95% by volume) was obtained from U.S. Industrial Chemicals (Louisville, Kentucky). Prime cottonseed containing 17.5% oil was obtained from California.

Hulling. The delintered seeds were hulled in Carver pilot plant equipment to yield a whole and cracked cottonseed meat fraction containing less than 3% hulls and 36.1% oil (dry basis). Meats were stored at −18 C until needed for extraction. Flakes approximately 0.26 mm thickness were obtained by processing thawed hulled meat fractions, without prior conditioning, through Allis Chalmers flaking rolls.

Drying. Flakes were dried below 2% moisture batchwise on trays in a forced draft oven at 82 C.

Extraction process. A flowsheet for the bench-top aqueous ethanol extraction process is shown in Figure 1. The charge to the 15 cm ID × 15 cm long, stainless steel extractor consisted of 500 g of cottonseed flakes containing approximately 2% moisture. The 20 mesh screened bottom, jacketed extractor and charge were brought up to an operating temperature of 79 C by circulating 79 C water in the jacket for 10 min. Approximately 1700 mL of boiling oil-lean miscella at 79 C were added to the flakes and the mixture was allowed to sit for 10 min. The oil-rich miscella was then drained for 1 min and chilled to 13 C while being pumped at about 175 mL/min through a 6.35 mm ID × 9 M aluminum coil immersed in a chilled water bath at 7 C. Chilled miscella containing free oil, emulsified oil and mucilaginous gum was then fed into a separating column (Fig. 2) very similar to one developed by Beckel et al. in their soy-aqueous ethanol research (11). Our phase separator is approximately 1.5 M high × 5.8 cm. ID with a total capacity of 4.3 liters and has both warm and chilled water jackets. Chilled miscella is fed into the column about 30 cm from the bottom, and free and emulsified oils fall and collect in the bottom of the column. The incoming mucilaginous gums agglomerate in the warm miscella and fall to the bottom of the column. The oil-lean miscella continually exits the top of the column. Free oil, emulsified oil, mucilaginous gums and a small amount of miscella exiting the bottom of the separator were homogenized with 35 mL of the 10% (w/w) caustic soda solution in a Waring laboratory blender for 3 min at high speed. The resulting solution at 43 C was centrifuged in 250 mL glass tubes at 2000 G's for 3 min in a size 2 International centrifuge. Centrifugation produced 3 distinct phases which were easily separated by siphoning. The refined and concentrated oil phase (middle) contained about 4% volatiles and was stripped of solvent in a rotary evaporator under reduced pressure (1 mm Hg) at 80 C until a constant weight was obtained. The oil fraction was then filtered and stored at 4 C until analyzed. The top miscella and bottom "foots" phases were combined, mixed

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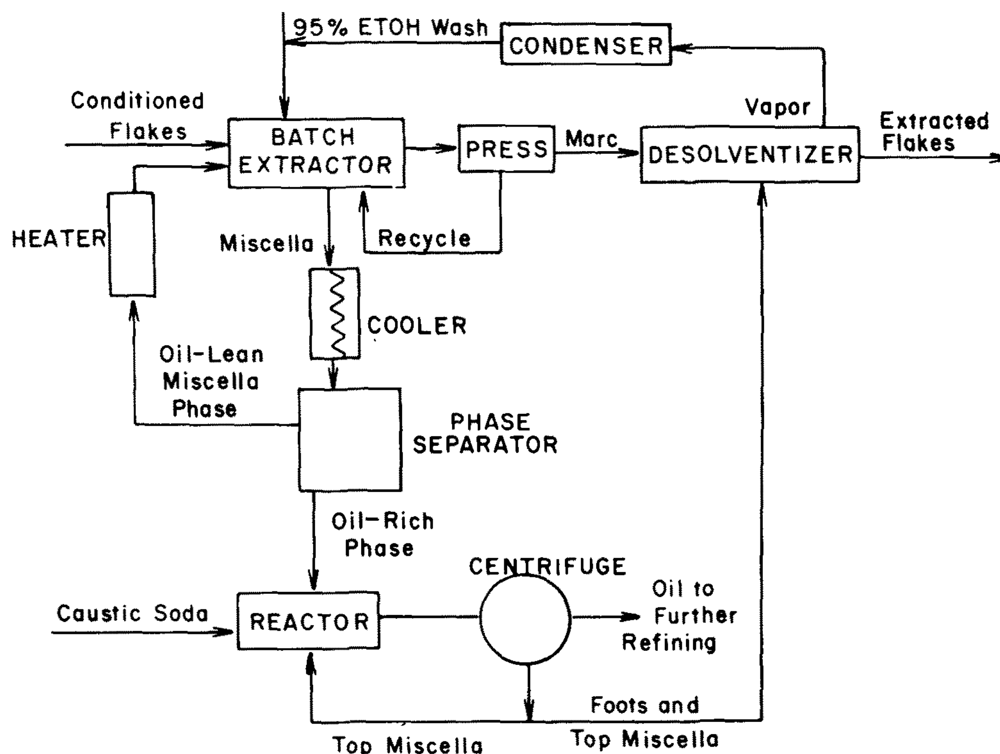

FIG. 1. Flowsheet for a cottonseed oil-aqueous ethanol extraction process.

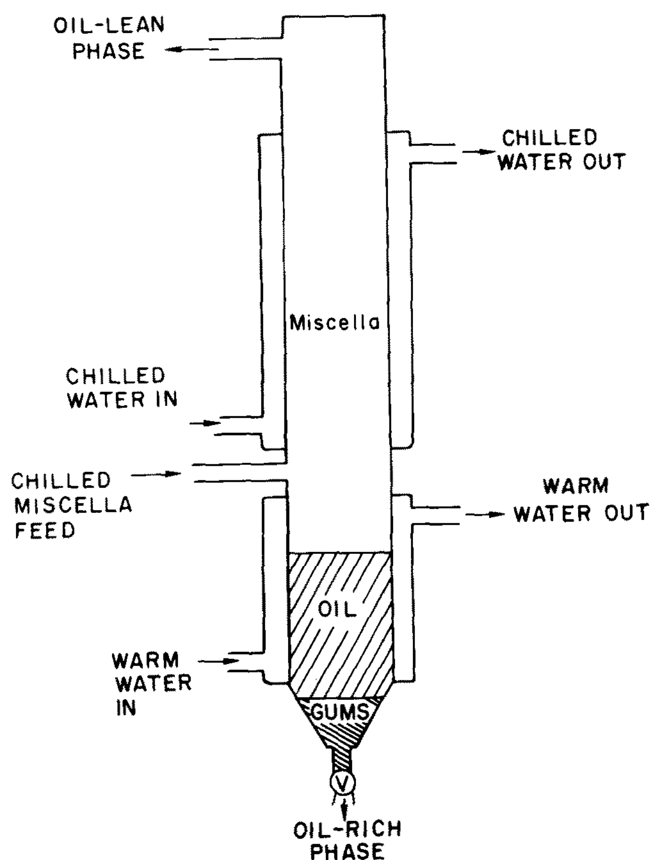

FIG. 2. Phase separation column.

and stoichiometrically added back to marc prior to its desolventization.

The oil-lean miscella overflowing the separating column was reheated to boiling and the extractor recharged (approximately 1200 mL). The flakes were allowed to soak for 10 min and then were drained. This cycle was repeated for a total of 8 times encompassing a period of roughly 90 min with the resulting miscella batches going through cooling operations to relieve them of their oil fractions. After the last draining, the marc was washed with 300 mL of 95% ethanol. This was considered to be roughly equivalent to what would be recovered from normal desolventization and stripping operations. After draining the wash, a weighed amount of marc (roughly ½ of the total), containing about 40% non-volatiles, was hydraulically pressed in a Carver Laboratory Press with a bore of 8.9 cm for 30 seconds at 873 kg force. This action roughly approximated that of a commercial press at 1379 kPa. Press liquor was recycled to the next extraction batch. After pressing, the marc contained about 60% non-volatiles. A stoichiometric amount of foots and top miscella from oil refining was added to the marc, which was desolventized first in ambient air overnight, and then in a forced draft oven at 82 C for 2 hours.

Analytical measurements. Moisture, nitrogen, fiber, ash, oils, free fatty acids, oil color, phosphorus and free gossypol were determined by standard AOCS methods (12). Carbohydrates were obtained by difference. Free sugars were analyzed by thin layer chromatography (TLC) (13). Total gossypol was determined by a modified AOCS method using 3-amino-1-propanol as described by Pons et al. (14). Nitrogen solubility was measured by dispersion in 0.02 N NaOH as suggested by Lyman et al. (15) and Martinez et al. (16). Refining loss was determined by modifying the AOCS method for 100 g samples.

RESULTS AND DISCUSSION

When hot miscella exiting the batch extractor was slightly cooled, a portion of the dissolved oil immediately became insoluble and separated as an emulsion. Further cooling to 38 C initiated gums separation with additional oil. Gums are not a serious problem in normal hexane-vegetable oil extraction processes, since their formation usually is confined to a controlled hydration step where they are precipitated and separated (17). However, gums obtained from alcoholic extractions generally are a mucilaginous material consisting of emulsified oil, phospholipids, pigments and sugars. They tend to settle into a third phase situated between oil and miscella, making a clean separation of miscella very difficult. At about 38 C, the gums lose some of their entrained miscella, agglomerate, and sink to the bottom of the oil phase. Therefore, it would be advantageous not to cool miscella below 38 C, thus avoiding gum formation altogether. But, this would result in high residual lipids in the marc. The problem was alleviated by constructing a phase separation column which, when fed a pre-chilled miscella, easily separated out a clear, overflow miscella phase ready for recycling (Fig. 2).

After more than 100 extraction runs, the equilibrium composition of the miscella was found to vary very little with an average non-volatile content of approximately 4.3%. Of this total, roughly 3.3% was a dark colored lipid-like material soluble in petroleum ether. The remaining 1.0% were ether insolbules consisting mostly of raffinose, stachyose and sucrose sugars. The miscella also contained 0.01% free and 0.01% total gossypol. The efficient separation of oil from gums in the oil phase exiting the separator has been a serious problem in most of the vegetable oil-ethanol extraction processes developed (11). The mucilaginous precipitate is a semi-solid material that readily blinds filters and plugs centrifuges, making them inoperable. Even when this material is separated from oil, it entrains large quantities of neutral oil because of its emulsified nature. Hexane miscella refining procedures can be adapted to this aqueous ethanol process to give a practical solution to the oil-gum separation problem (18). Homogenizing the total oil-rich stream of miscella and gums exiting the separator and treating it with caustic soda causes the resulting solution to break in a few minutes, as in the hexane process. Then it can be centrifuged into two or three distinct phases, which is unique to this process. A three-phase system consists of clear miscella, refined concentrated oil and semi-solid "foots," from top to bottom, respectively. A two-phase system consisting of refined oil and liquified "foots" forms if an excess of water is present. Water increases the density of the miscella phase until it exceeds that of the oil phase, whereupon the miscella sinks and mixes with and liquifies the foots. The use of a three-phase system provides an additional benefit not available in hexane miscella refining in that foots can be washed with the top miscella phase and recentrifuged to optimize refined oil recovery. The resultant foots either can be added back directly to the marc prior to desolventization or stripped of its alcohol and concentrated prior to add back. Table I shows the analyses of oils obtained by hexane and 95% ethanol extractions of the same seed. The second sample was crude oil stripped of ethanol and filtered to remove precipitated sugars and gums prior to being refined. The third sample was an oil refined as previously described and then refined again using a modified AOCS procedure. Although Karnofsky reported obtaining light yellow colored, semirefined oils directly from ethanol extractions (9), this process' crude oils were reddish brown, contained approximately 0.01% free gossypol and 0.04% total gossypol and were only slightly lighter than the hexane extracted control. The extraction of pigments probably was due to the use of the same miscella in over 100 extraction runs during a 9-month period. Thus, these results are indicative of what could be expected from commercial operations using miscella recycling techniques. However, even under drastic conditions, ethanol extracted crude oil had a low refining loss, and both experimental samples produced light-colored, refined and bleached oils.

Figure 3 shows how residual lipids in the marc vary with extraction stages at a chill temperature of 13 C. The three curves show, from top to bottom, residual lipids in marcs after gravity draining, after washing and draining, and after pressing washed and drained marc. After fifteen 10-minute extractions, the residual lipids in the marc could not be

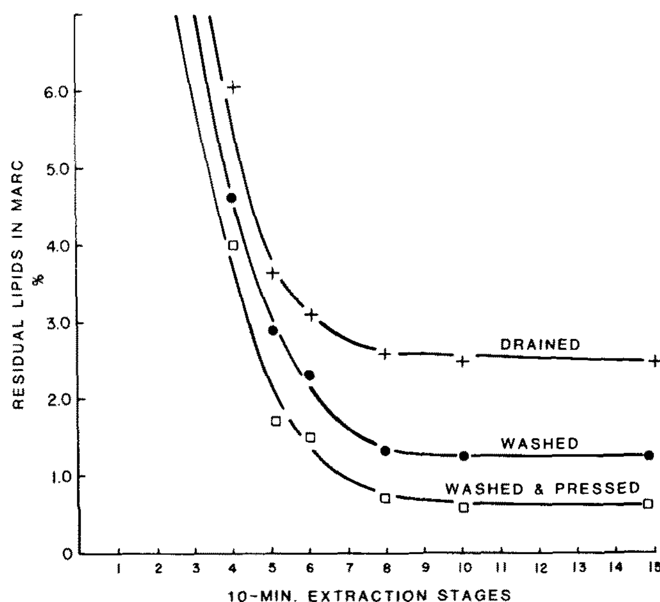

FIG. 3. Effect of washing and pressing on marc residual lipids.

TABLE I

Analysis of Crude and Refined Cottonseed Oil Extracted with 95% Aqueous Ethanol

	FFA[a] (%)	Refining loss (%)	Refined color[b]	Bleached color[b]	Phosphorus (ppm)
Hexane extracted crude oil control	0.5	2.2	35Y 4.0R	16Y 1.6R	110
95% ETOH extracted crude oil	0.3	1.6	35Y 4.3R	23Y 2.3R	120
95% ETOH extracted and refined oil	trace	–	35Y 3.0R	13Y 1.3R	2.3

[a]FFA = Free Fatty Acid.

[b]Lovibond colors.

TABLE II

Analyses of Desolventized Cottonseed Meals

	Lipids (%)[a]	Protein (%)[b]	Carbohydrates (%)[a]	Gossypol Free (%)[a]	Gossypol Total (%)[a]	Nitrogen solubility (.02N NaOH) (%)
Hexane extracted meal control	0.44	64.5	24.4	1.01	1.06	98.6
95% ETOH extracted meal	0.75	68.8	19.0	0.08	1.08	70.4
95% ETOH extracted meal plus "foots"	0.77	65.6	21.7	0.07	1.26	61.5

[a]As-is basis.
[b]Moisture-/ and oil-free basis, N × 6.25.

reduced below 2% without washing or below 1% without pressing because of the petroleum ether soluble, lipid-like material in the recycled miscella. Since very little difference was noted in residual lipids after 8 extractions at a chill temperature of 13 C, this was chosen as a standard. This temperature is not necessarily optimum, but due to equipment limitations, it was the lowest reproducible temperature obtainable. Although pressing is an energy intensive operation, Sullivan et al. recently pointed out that with pressing, the total energy consumed in desolventization in an alcohol process is significantly less than the total energy used in the miscella evaporation and desolventization steps of a hexane process (19). Miscella evaporation, an energy intensive operation, is required in hexane processing but is not needed in an alcohol process.

The proximate analyses of a hexane extracted control meal without foots add back and ethanol extracted meals with and without foots add back are shown in Table II. Moisture free and oil free protein contents of the meals are higher than usual since only whole and cracked meat fractions were used in the extractions. This was done to minimize the possible effect of hull segregation on the analyses. The 95% ethanol extracted meal is highest in protein, due to some carbohydrate extraction, indicated by the correspondingly lower carbohydrate content. However, after foots add back, the ethanol and hexane extracted meal protein levels are within experimental error.

In hexane processing, to convert free gossypol to the bound form during "cooking," kernel moisture content exceeding 9% and processing temperatures above 115 C must be attained (20). Free gossypol was reduced noticeably in ethanol extracted meals even though 2% moisture flakes were used and processing temperatures did not exceed 82 C. Furthermore, we have observed that aqueous ethanol will easily convert free gossypol to bound gossypol even under ambient conditions, regardless of kernel moisture. To extract significant quantities of gossypol from cottonseed, dilute alcohols are needed, as shown by Karnofsky (9). The high total gossypol level of 1.26% contained in the ethanol extracted meal was due to adding back "foots." The foots contained all of the precipitated gums whose free and total gossypol contents before refining were 0.14% and 0.25%, respectively.

The absence of high moisture and excessive heat in processing these meals is also evidenced by the high nitrogen solubility of the hexane extracted meal. The nitrogen solubility of commercially extracted cottonseed meals normally ranges from 60 to 70%, which is similar to the values that were obtained for ethanol extracted meals (21).

Although nitrogen solubilities of bench-top ethanol extracted meals, produced under mild laboratory conditions, are comparable with commercial hexane extracted meals, produced under much more severe conditions, it is yet to be determined what nutritional relationships exist.

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