Cottonseed Extraction with Mixtures of Acetone and Hexane

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ABSTRACT: Cottonseed flakes were extracted with mixtures of *n*-hexane and acetone, with the concentration of acetone varying between 10 and 75%. Adding small amounts of acetone (≤25%) to *n*-hexane significantly increased the extraction of free and total gossypol from cottonseed flakes. Sensory testing detected no difference in the odor of cottonseed meals produced either by extraction with 100% *n*-hexane or by extraction with a 10:90 (vol/vol) mixture of acetone/hexane. More than 80% of the free gossypol was removed by the 10:90 mixture of acetone/hexane, whereas pure *n*-hexane extracted about 47% of the free gossypol from cottonseed flakes. A solvent mixture containing 25% acetone removed nearly 90% of the free gossypol that was removable by extraction with pure acetone; the residual meal had only a minimal increase in odor. In contrast, cottonseed meals produced by extraction with pure acetone had a much higher odor intensity. The composition of the cottonseed crude oil was insignificantly affected by the acetone concentration of the extraction solvent. The results indicate that mixtures of acetone and *n*-hexane can be used as extraction solvents to produce cottonseed crude oil without the concomitant development of odorous meals.

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KEY WORDS: Cottonseed oil, hexane and acetone mixtures, meal, odor, quality, solvent extraction.

Although cottonseed meal is valuable as animal feed, the use of cottonseed meal is limited by the presence of free and total gossypol (1). Extraction of cottonseed with either ethanol or isopropyl alcohol has previously been studied (2,3), in part to test the potential of these alternative extraction solvents to remove gossypol. Although the technical viability of the extraction process with alcohols was established, the cost of the alcohol extraction process made the process economically unfeasible (4). The main difficulties were the energy required for the evaporation of isopropyl alcohol or ethanol and the necessity of working around a water–alcohol azeotrope to remove co-extracted moisture. Early work with acetone showed it to be a suitable oilseed extraction solvent that could also extract gossypol from cottonseed (5). However, acetone-extracted cottonseed meal has a pronounced "catty odor" that may limit its feeding potential (6). Reduction of the seed moisture content has been suggested to reduce this problem. However, the high costs associated with drying seed to a low enough moisture level make this solution economically unfeasible.

In this study mixed solvents that use a relatively small amount of acetone in hexane were considered for the extraction of oil and gossypol from cottonseed. The study also aimed to investigate whether cottonseed meal without the catty odor can be produced by extraction with a solvent mixture containing reduced amounts of acetone.

MATERIALS AND METHODS

All extractions were conducted in duplicate with a Soxhlet apparatus. Recently harvested cottonseed was flaked with a roller to a thickness of 0.008 ± 0.001 in. and conditioned to a final moisture level of 6.5 ± 0.5%. Extractions were conducted on samples of 50 ± 0.5 g with 400 mL of extracting solvent for 4 h. Reagent-grade *n*-hexane and acetone (J.T.Baker, Phillipsburg, NJ) were used.

After extraction, flakes were ground in a laboratory mill to pass a 1-mm sieve after first drying overnight in a hood and further drying 2 to 4 h at 101°C in a draft oven until the flake weight became invariant. Total and free gossypol in the meal was determined by AOCS official methods (6). The ground meal was then sieved over a 20-mesh screen (850 μm opening) to ensure the samples had similar particle sizes and surface-to-mass ratios. The through-particles were further dried at 101°C for 2 h in a draft oven and evaluated by a sensory panel.

Extracting solvent was removed from the crude oil using a laboratory-scale rotating film evaporator that was operated under vacuum. To ensure the complete removal of the solvent, the evaporation process was continued until the weight of oil became invariant. The color of crude oil and total gossypol and FFA levels were determined by AOCS methods (7). The content of phosphorus was determined to estimate the phospholipid contents in the crude oil by inductively coupled plasma atomic absorption after acid digestion by ASTM methods (8). The FA, glyceride, and glycerol composition of the extracted oil was determined by capillary GC after trimethylsilyl derivatization. The silylation procedure and GC conditions were described previously (9).

RESULTS AND DISCUSSION

Commercial hexane is an efficient solvent for extracting TAG from oilseeds, but for cottonseed extraction, its nonpolarity limits the removal of hydroxylated compounds such as gossypol. Gossypol is considerably more polar than TAG, as indicated in the Hildebrand solubility analysis of lipids in edible oils (10). The use of isopropyl alcohol or ethanol as extraction solvent, which would be useful for extracting oil and gossypol, would result in some significant investment costs to retrofit the current oil processing facilities because of the azeotropic distillation that would be required to remove co-extracted water. To

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TABLE 1
Oil Yield, Odor Intensity, and Total and Free Gossypol Concentration in Cottonseed Meals Produced by Extraction with Various Acetone/Hexane Mixtures

Mixture volume (%) acetone/hexane	Extraction oil yield (5)	Catty odor intensity[b]	Gossypol[a] Total[c]	Free[d]
0:100	34.6	0	0.91	0.37
10:90	35.1	0	0.57	0.12
25:75	34.4	2.0	0.43	0.08
50:50	36.1	6.0	0.40	0.06
100:0	34.1	6.0	0.40	0.05

[a] Raw flakes contained 1.01% total and 0.7% free gossypol.
[b] The scale in Reference 11 was used.
[c] Determined using AOCS Official Method Ba 7-58 (7).
[d] Determined using AOCS Official Method Ba 8-78 (7).

improve the solubility limitations of hexane, solvent mixtures of hexane containing either alcohols or acetone may be useful.

Unlike alcohols, acetone does not form an azeotrope with water, and the heat of vaporization for acetone is about equal to that of *n*-hexane. Hence, the energy cost for the solvent recovery, part of an acetone or an acetone/hexane process, would be comparable to the hexane process. Considering the complete miscibility of acetone with *n*-hexane, and the high solubility of gossypol in acetone (11), acetone/hexane would be a workable solvent system to process cottonseed, if a meal can be produced without a detrimental odor problem.

As seen in Table 1, the oil extraction yields were invariant at 35 ± 1% regardless of the acetone concentration in the solvent mixture. However, total and free gossypol levels in the meal changed significantly with increased acetone concentration. More than 50% removal of total gossypol and 90% removal of free gossypol were achieved by extraction with the solvent mixture containing 25% acetone. The solvent mixture with 10% acetone removed less free gossypol than the solvent mixture containing 25% acetone. Nevertheless, the removal of more than 80% of the meal free gossypol and 40% of the meal total gossypol by extraction with the solvent with 10% acetone was achieved, confirming the strong influence of a small amount of acetone on the solubility of gossypol (11). The characteristic catty odor was not detected in the meal produced with a mixture of 10% acetone in hexane. The odor intensity of meal produced with 25% acetone was evaluated as 2 (see Ref. 12 for a description of the intensity range). In comparison, the meal produced by extracting with pure acetone had a strong catty odor with an intensity level of 6, a value that is considered strong enough to pose a problem as animal feed. These data indicate the acetone concentration maximum that would produce cottonseed meal without the detrimental odor lies in the range of 10 to 20%.

A summary of crude oil composition is given in Table 2, and the results of proximate analyses on the extracted crude oils are shown in Table 3. Since the meal produced with solvent having higher than 50% acetone had the strong odor, properties are reported only for the crude oils produced with an acetone concentration ≤50%. As seen in Table 2, the crude oil compositions varied insignificantly with the acetone concentration of the solvent mixture. A small increase in FFA concentration (up to 1%) and a trace increase in glycerol were observed with the acetone addition of ≤50%. The amount of FFA in crude oils extracted by the solvent mixtures was slightly higher than that by 100% hexane solvent. The total concentrations of TAG (with carbon numbers 48, 50, 52, and 54) in crude oils produced by the acetone/hexane mixtures were reduced by 3 to 4% compared with that by pure hexane. Since the solvent containing acetone is more polar than pure hexane, more polar compounds such as FFA were extracted by the acetone/hexane solvent than 100% hexane, contributing to a reduction in the total concentration of TAG. This phenomenon, reduction in the total concentration of TAG with the addition of acetone to hexane, is

TABLE 2
Composition Summary of Cottonseed Crude Oils Produced by Extraction with Acetone/Hexane Mixtures

Compound	Extraction mixture (acetone/hexane, vol/vol %) 25:75	50:50	0:100
FFA[a]	9.3	8.7	8.3
Glycerol	≥0.04	≥0.02	≥0.01
Sterol (β-sitosterol)	0.3	0.3	0.2
DAG[b]	6.4	6.4	6.0
TAG[c]	82.7	83.9	87.2

[a] Composed of palmitic, linoleic, and oleic acids.
[b] With two acyl chains consisting of palmitic, stearic, oleic, or linoleic acid.
[c] With three acyl chains consisting of palmitic, stearic, oleic, or linoleic acid.

TABLE 3
Proximate Analyses of Cottonseed Crude Oils Produced by Acetone/Hexane Extraction

Mixture volume (%) acetone/hexane	Color[a,b] Red	Color[a,b] Yellow	FFA[b,c] (%)	Phosphorus[d] (ppm)
0:100	2.0	12.9	5.1	731
10:90	11.5	16.8	5.5	726
25:75	11.6	69.0	5.6	891
50:50	11.9	70.6	5.6	1050

[a] AOCS Official Method Cc13e-92 (7) with 2.5 mm cell.
[b] 50% oil in miscella (miscella recovered by a laboratory evaporator was added).
[c] Measured as oleic acid equivalent by AOCS official method Ca 5a-40 (7).
[d] Inductively coupled plasma coupled with atomic adsorption after acid digestion.

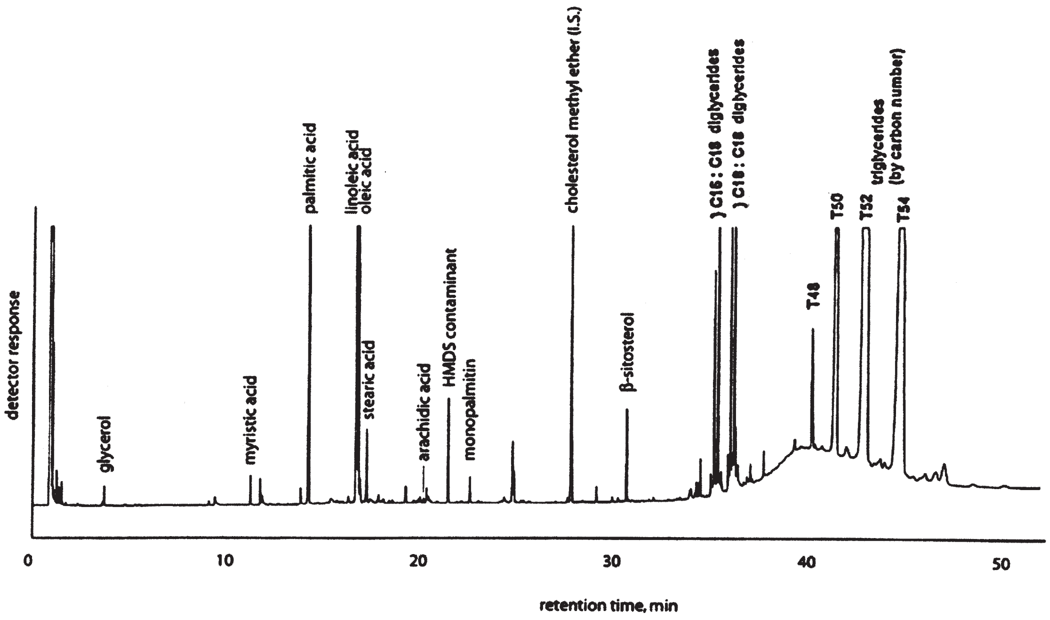

FIG. 1. Gas chromatogram of trimethylsilyl-derivatized cottonseed crude oil produced by extracting with a 50:50 (vol/vol) mixture of acetone/*n*-hexane.

expected, as suggested in the literature (10). A typical chromatogram of a silylated cottonseed crude oil produced with the solvent mixture (50% acetone) is shown in Figure 1. A few minor FFA such as myristic and arachidic acid were excluded from the summary of crude oil composition (Table 2) because of their negligible contribution, as shown in Figure 1.

The amount of phospholipids in the crude oil, which is directly proportional to the content of elemental phosphorus (13), varied slightly depending upon the acetone concentration. However, the crude oil colors varied significantly with the acetone concentration. The crude oil increased in "redness" as the acetone concentration in the extraction solvent increased. A positive correlation appeared to exist between the acetone concentration and the value of yellow color. The positive correlation may be attributable to the color of pure gossypol, which is bright yellow. The increasing color intensity in relation to total gossypol in the crude oils indicates that extra refining steps may be required. These extra refining steps are especially necessary for crude oil produced by mixed solvents containing an acetone concentration greater than 25%.

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