SHORT COMMUNICATION

Hexane and Heptane as Extraction Solvents for Cottonseed: A Laboratory-Scale Study

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ABSTRACT: For many years, commercial-grade hexane has been the preferred solvent for extracting oil from cottonseed. Recent environmental and health concerns about hexane may limit the use of this solvent; therefore, the need for a replacement solvent has become an important issue. Heptane is similar to hexane, but does not have the environmental and health concerns associated with the latter. On a laboratory scale, delinted, dehulled, ground cottonseed was extracted with hexane and heptane. The solvent-to-meal ratio was 10:1 (vol/wt). The yield and quality of the oil and meal extracted by heptane were similar to that extracted by hexane. Extraction temperature was higher for heptane than for hexane. A higher temperature and a longer time were required to desolventize miscella from the heptane extraction than from the hexane extraction. Based on these studies, heptane offers a potential alternative to hexane for extracting oil from cottonseed.

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KEY WORDS: Cottonseed, extraction, heptane, hexane, solvents.

For many years, commercial-grade hexane has been the solvent of choice for extraction of oil from cottonseed. However, pending legislation may result in a costly investment in new control technologies for hexane users because of environmental and health concerns about the solvent (1). Cottonseed processors, therefore, have become interested in developing alternate solvent systems for oil extraction. The ideal system would be one that uses a nontoxic low-volatility solvent, extracts the same amount of oil as hexane, has no adverse effect on oil or meal quality, and requires minimum retrofitting of the oilseed processing plant. None of the systems investigated to date meet all these requirements. In 1992, discussions with representatives of Texaco Chemical Co. (Houston, TX) led us to consider heptane as an alternate solvent. Heptane does not have the environmental and health concerns that are associated with hexane (2), and, because of the similarity of the solvents, only minimal changes in the processing plant should be needed. Heptane could be an immediate alternative solvent for the cottonseed industry.

As early as 1937, MacGee (3) noted that the best petroleum solvents for oilseed extraction were the narrow-boiling range hexane and heptane fractions. This was based on stability, odor, and taste of the products, low evaporation loss of solvent, and lack of corrosion and greasy residue in the equipment. Ayers and Dooley (4) extracted cottonseed on laboratory scale with various solvents, including commercial-grade and high-purity hexane and heptane. The amount of oil extracted by each solvent was similar, but refining losses and oil colors varied. They also noted that oil color differences were dependent on the free fatty acid (FFA) content of the seed. In general, the color of the hexane-extracted oils was more intense than that of the heptane-extracted oils. Johnson and Lusas (5) reported that oils extracted with heptane were more difficult to desolventize than those extracted with hexane. The amount of phospholipids extracted with heptane was significantly higher than that extracted with hexane (6). None of these reports compared the qualities of the meals extracted with these solvents. This paper compares the yields and qualities of oils and meals from two cottonseed samples extracted on laboratory scale with hexane and heptane.

EXPERIMENTAL PROCEDURES

Cottonseed was provided by Yazoo Valley Oil Mill (Greenwood, MS) from the 1991 crop grown in the Mississippi Delta. Two samples of seed with different FFA content were used: **I** <2% FFA and **II** >2% FFA. The fuzzy seed was delinted and dehulled, and the kernels were stored at 4°C. Immediately before extraction, the kernels were ground to pass a 20-mesh screen.

Solvents were supplied by Texaco Chemical Co.: hexane, Texsolve B, and two heptanes, Texsolve C and E. The solvent characteristics and compositions are listed in Table 1.

Two extraction systems were used: the Soxtec System HT6 (Perstorp Analytical, Herndon, VA) and a conventional Soxhlet extraction unit. A solvent-to-meal ratio of 10:1 (vol/wt) was used in both systems, with 3 g of meal per thimble in the Soxtec and 60 g of meal in the Soxhlet. Condensers for both systems were maintained at 15°C. In the Soxtec, reflux temperature was set at 160°C for hexane and 180°C for the heptanes; extraction time was 15 min, followed by rinsing for 35 min. In the Soxhlet, extraction temperature

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TABLE 1
Properties and Composition of Solvents Used for Extraction of Oil from Cottonseed

	Texsolve B (hexane[a])	Texsolve C (heptane[a])	Texsolve E (heptane[b])
Boiling range (°C)	68–70	88–95	88
Density (g/mL) (16°C)	0.677	0.698	0.694
Heat of vaporization (cal/mol)[c]	7,121	7,519	7,649
Composition			
n-Hexane	80–95%	3–11%	< 1%
n-Heptane		80–95%	80–95%
Methylcyclopentane	11–20%		
n-Octane		1–3%	3–11%
Toluene		1–3%	< 1%
Cyclohexane		1–3%	
Benzene		< 1%	

[a]Commercial-grade. Texsolve B, C, and E (Texaco Chemical Co., Houston, TX).
[b]High-purity.
[c]Calculated, based on the two major components of each solvent (Ref. 9).

was the boiling point of the solvents, and extraction time was 4 h.

Extracted oil and meal samples were desolventized in a vacuum oven to determine yield. FFA contents and refining losses of the oils, and nitrogen and gossypol contents of the meals were determined by Official AOCS Methods, with appropriate modification for sample size (7). Lovibond oil color was measured in a 10-mm cell in a Colourscan apparatus (Tintometer, Salisbury, England). Fatty acid methyl esters (FAME) were prepared by basic methylation according to Christie *et al.* (8). However, benzene was used to solubilize the oils and, for injection into the gas chromatograph, the FAME were suspended in hexane/isopropanol (90:10). A Hewlett-Packard gas chromatograph, 5890, Series II (Avondale, PA) was used. The column was a fused-silica capillary (SP-2380; Supelco, Inc., Bellefonte, PA). Conditions were: injector and flame-ionization detector (FID) at 200°C; oven temperature programmed from 130–145°C at 5°C/min; 145–200°C at 10°C/min; and carrier gas, helium at 8 mL/min. After digestion of the oils in a sulfuric acid/peroxide system, phosphorus analyses were conducted with the Plasma spectrophotometer (ICP; Leman Labs, Lowell, MA). Amino acid contents of the meals were determined by a commercial laboratory using ion-exchange chromatography with post-column derivatization on a Beckman Model 126AA System (Fullerton, CA).

For refining and desolventizing studies, miscellas from the Soxhlet extractions were diluted to 60% oil/40% solvent. Samples, 20–30 g, of the miscellas were refined with 51% NaOH diluted to 20° Baume. Desolventization times and solvent recoveries were determined in a rotatory evaporation system.

RESULTS AND DISCUSSION

In the initial phase of this study, two cottonseed samples were extracted with the conventional solvent, commercial-grade hexane, and with two alternate solvents, commercial-grade and high-purity heptane. In the Soxtec system, it was determined that yields of oils and meals from the two cottonseed samples were similar for all three solvents (Table 2). Total material recovery was 91% for Texsolve B, and 89 and 90% for Texsolve C and E, respectively.

Oils extracted from Sample **I** with Texsolves B, C, and E contained 1.49, 1.47, and 1.58% FFA, respectively. Oils extracted from Sample **II** with the solvents contained 2.45, 2.47, and 2.92% FFA, respectively. All oils had fatty acid profiles that are typical of cottonseed oil, and the saturated to unsaturated ratios ranged from 0.34 to 0.40. Phosphorus contents of the oils extracted with Texsolves B and E were 632 ± 25 and 629 ± 29 ppm, respectively. Phosphorus content of the oil extracted by Texsolve C was 829 ± 31 ppm.

Meals from cottonseed Sample **II** contained slightly more protein and slightly less gossypol than meals from cottonseed Sample **I** (Table 3). There were no differences noted, however, with respect to solvents for protein and gossypol contents. Similarly, while amino acid profiles of the meals varied slightly, there was no apparent solvent effect (Table 4).

From the information gained by Soxtec extraction, hexane and both heptanes extract similar amounts of oil from cottonseed meals of differing quality. Oil quality with respect to FFA was similar for all extracting solvents. There was an indication that Texsolve C extracted more phosphorus than either of the other solvents. This may have been due to one or more of the impurities in Texsolve C. There is, also, no apparent change in meal quality when heptane is substituted for

TABLE 2
Yields[a] of Oil and Meal from Soxtec Extraction of Two Cottonseed Samples with Hexane and Heptane

	Sample I		Sample II	
Solvent	Oil	Meal	Oil	Meal
Texsolve B	32.1 ± 0.09	59.5 ± 0.65	28.4 ± 0.36	62.5 ± 0.52
Texsolve C	32.3 ± 0.08	54.4 ± 1.15	30.4 ± 0.19	59.3 ± 0.53
Texsolve E	32.4 ± 0.19	56.5 ± 1.93	29.6 ± 0.40	61.6 ± 0.85

[a]Average of six determinations. See Table 1 for company source and address.

TABLE 3
Protein and Gossypol Contents of Meals from Two Cottonseed Samples Extracted with Hexane and Heptane in the Soxtec System

	Protein[a]		Gossypol[b]	
Solvent	I	II	I	II
Texsolve B	53.4	55.9	2.13	1.93
Texsolve C	53.7	57.4	2.04	1.94
Texsolve E	53.7	56.9	2.08	1.99

[a]%N × 6.25, Average SD %N = ± 0.07. See Table 1 for company source and address.
[b]Average SD ± 0.03.

TABLE 4
Essential Amino Acid Contents[a] of Meals from Two Cottonseed Samples Extracted with Hexane and Heptane (g/100 g meal)

	Texsolve B		Texsolve C		Texsolve E	
Amino Acid	I	II	I	II	I	II
Threonine	2.41	2.74	2.52	2.45	2.49	2.41
Valine	3.04	3.54	3.12	3.06	3.04	2.92
Methionine	1.36	1.50	1.45	1.42	1.43	1.37
Isoleucine	2.24	2.43	2.30	2.26	2.26	2.17
Leucine	4.20	4.84	4.47	4.39	4.36	4.32
Phenylalanine	3.87	4.62	4.00	4.11	3.97	3.94
Lysine	2.92	3.20	3.10	2.88	2.91	2.78
Histidine	2.03	2.38	2.13	2.18	2.11	2.11
Arginine	8.26	9.99	8.57	9.04	8.42	8.97

[a]Average SD ± 0.3. See Table 1 for company source and address.

hexane. The major difference was the need for a higher reflux temperature with heptane.

Insufficient oil was obtained by the Soxtec extraction to allow a study of oil quality, i.e., color, refining loss, and desolventization. Therefore, a traditional Soxhlet extraction was set up in which 60 g rather than 18 g of kernels could be extracted. The above data showed that initial cottonseed quality was not a factor and that Texsolve C and E were equivalent except for phosphorus removal. Therefore, for this phase of the study, cottonseed Sample **II** and Texsolves B and E were used.

Oil extracted with Texsolve B contained 2.7% FFA, while that extracted with Texsolve E contained 2.5%. Desolventization of the oils was simulated in the laboratory with a rotary evaporator. With the bath temperature set at 58°C, the condenser at 5°C, and the system under 1/2 atm pressure, 14 min were required to recover 77% of Texsolve B from the oil. For Texsolve E, it was necessary to set the bath temperature at 64°C. It required 28 min to recover 78% of the solvent. Data in Table 5 indicate no difference in color of either crude or refined oils extracted from cottonseed Sample **II** with hexane or heptane.

TABLE 5
Colors of Crude and Refined Oils Extracted with Hexane and Heptane from Cottonseed Sample II[a]

Solvent	Crude	Refined
Texsolve B	9.0 R, 67.0 Y	1.3 R, 10.5 Y
Texsolve E	9.4 R, 69.0 Y	1.6 R, 11.7 Y

[a]See Table 1 for company source and address; R = red; Y = yellow.

Results from this study indicate that the yield and quality of meal and oil removed from cottonseed by heptane are equivalent to that of the meal and oil removed by hexane. The major disadvantage for oilseed processors is increased energy use, i.e., higher extraction temperature for heptane and the increased amount of heat required to desolventize the miscella and marc from the heptane extraction as compared with that from the hexane extraction. To determine the changes in economic costs, pilot-plant or mill-scale studies must be conducted. It is conceivable, however, that heptane could be substituted for hexane in cottonseed processing plants with limited retrofitting of the equipment. Heptane, therefore, offers a potential alternative to hexane for cottonseed processing.

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