Alternative Hydrocarbon Solvents for Cottonseed Extraction[1]

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ABSTRACT: Hexane has been used for decades to extract edible oil from cottonseed. However, due to increased regulations affecting hexane because of the 1990 Clean Air Act and potential health risks, the oil-extraction industry urgently needs alternative hydrocarbon solvents to replace hexane. Five solvents, *n*-heptane, isohexane, neohexane, cyclohexane, and cylopentane, were compared with commercial hexane using a bench-scale extractor. The extractions were done with a solvent to cottonseed flake ratio of 5.5 to 1 (w/w) and a miscella recycle flow rate of 36 mL/min/sq cm (9 gal/min/sq ft) at a temperature of 10 to 45°C below the boiling point of the solvent. After a 10-min single-stage extraction, commercial hexane removed 100% of the oil from the flakes at 55°C; heptane extracted 100% at 75°C and 95.9% at 55°C; isohexane extracted 93.1% at 45°C; while cyclopentane, cyclohexane, and neohexane removed 93.3, 89.4, and 89.6% at 35, 55, and 35°C, respectively. Each solvent removed gossypol from cottonseed flakes at a different rate, with cyclopentane being most and neohexane least effective. Based on the bench-scale extraction results and the availability of these candidate solvents, heptane and isohexane are the alternative hydrocarbon solvents most likely to replace hexane. *JAOCS 72*, 653–659 (1995).

KEY WORDS: Alternative solvents, cottonseed, cyclohexane, cyclopentane, extraction, extraction efficiency and rate, heptane, hexane, hydrocarbon solvents, isohexane, miscella, miscella concentration, neohexane.

Hexane has been used as an extraction solvent for cottonseed oil for more than half a century. Because hexane is extremely flammable and nonbiorenewable, several groups in the United States have devoted major efforts in the search for an alternate solvent during the past 10–15 years. Ethanol (1) and isopropanol (2) have been the main focus. Processes using these solvents have been developed; however, neither solvent presently is considered economically feasible as a suitable replacement for hexane (1).

With increased federal regulation of hazardous air pollutants (HAP) and volatile organic compounds (VOC) under the 1990 Clean Air Act (CAA) (3,4), the oilseed processing industry faces increasing pressure to control the loss of hexane. Commercial hexane emitted from oilseed extraction is a source of VOC, which are ozone precursors. Ozone is a regulated criteria pollutant and if 100 tons per year (tpy) of VOC per plant are emitted, the plant is a major source. The main component of commercial hexane, *n*-hexane, is listed as 1 of 189 HAP, and vegetable-oil processing is listed as a source category for hexane emissions. If a source emits 10 tpy of an HAP or 25 tpy of total toxic pollutants, it is a major source requiring a Federal Operating Permit (FOP). Assuming that an average loss of hexane is one-half gallon per ton of cottonseed crushed, then plants with an average daily processing capacity of about 50 tons or more will exceed the 10 tpy threshold. Therefore, most oil mills using hexane would have to get a FOP and pay an annual fee of at least $25/ton of hexane lost; this will be required as early as the end of 1994 in some locations.

Until an environmentally friendly solvent becomes economically feasible for the cottonseed extraction industry, it seems logical that a search be made for an alternate hydrocarbon solvent which poses less of a health risk than *n*-hexane. Various alternative solvents for oil extraction have been reviewed by Hron *et al.* (5) and Johnson and Lusas (6) in the early 1980s. Prior to that, a thorough comparison of various hydrocarbon solvents for cottonseed oil extraction on a lab-scale basis was reported by Ayers and Dooley in 1948 (7). Among the petroleum hydrocarbon solvents tested by Ayers and Dooley were branched, normal, and cyclo-paraffins, as well as aromatic hydrocarbons. They concluded that methylpentanes were superior solvents for cottonseed oil extraction. However, their work was done either in a Soxhlet extraction at the boiling points of selected solvents or with a Waring blender at room temperature.

In the newest research, the extraction characteristics of several commercial-grade solvents, not listed as HAP under CAA and considered as less of a health risk than *n*-hexane (8), were investigated. The study was done using a bench-scale extractor that closely simulates the commercial operating conditions in terms of extraction temperature, time, miscella (mixture of oil and solvent) recycling rate, and various starting miscella concentrations (% oil in miscella by weight) of each solvent. The quality of oils extracted by these solvents was also evaluated.

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EXPERIMENTAL PROCEDURES

Mill-run cottonseed meats of the 1992 crop season obtained from a Mississippi oil mill (Greenwood, MS) were sieved through an 8-mesh screen to remove fines. Water was added to the meats, which then were conditioned at room temperature overnight to achieve a moisture level of 14%. The meats were then flaked to 0.254 mm (0.01 inch) thickness using Ross Flaking Rolls (Ferrell-Ross, Bluffton, IN). The flakes were immediately dried in a forced draft oven at 71.1°C (160°F) until a 5.8% moisture was obtained and then stored at –20°C. The flakes contained 31.4% extractable oil (as is or wet basis) as determined by the Soxhlet extraction procedure.

Six hydrocarbon solvents, hexane (Control), heptane, isohexane, neohexane, cyclohexane, and cylopentane, were used in the extraction study. Hexane and heptane were supplied by Texaco Chemical Company (Houston, TX) with the trademark of Texsolve B and Texsolve E, respectively. The other four solvents were provided by Phillips Petroleum Company (Bartlesville, OK). Chemical composition and some selected physical properties for these solvents are given in Tables 1 and 2.

Extraction of cottonseed flakes at the boiling point of each solvent was done with a Soxtec System HT 1043 Extraction Unit (Tecator, Sweden) according to the following procedure. Three grams of cottonseed flakes were precisely weighed and placed in a thimble, which was lowered into a flask containing 30 mL solvent. The flakes were submerged and extracted in the boiling solvent for 15 min. The thimble was then raised above the solvent flask and rinsed by the condensed solvent for 35 min. The oil in the flask was desolventized in the unit and then in an oven at 130°C for one hour to obtain the net weight of oil extracted.

For the bench-scale extraction study, the extractor was similar to that described by Abraham *et al.* (9) except that the flakes were contained in a solid stainless cylinder with a 20-mesh wire screen at the bottom instead of stainless-steel wire screen cylinder wall. A schematic of the extractor appears in Figure 1. The temperature of the miscella and the entire extractor was controlled within ±0.5°C. Extraction conditions used for this study were (i) to minimize vaporization loss of solvent and maintain a temperature close to that of industrial operation; the extraction temperature was set at 10–45°C below the boiling point of each solvent; (ii) 100 g of cotton-

TABLE 1
Chemical Composition of Selected Hydrocarbon Solvents (wt%)

	Types of solvent					
Chemical component	Hexane	Heptane	Isohexane	Neohexane	Cyclohexane	Cyclopentane
Cyclohexane		0.8			98.8	
Cyclopentane						77.5
2,2-Dimethylbutane			12.2	99.5[a]		11.7
2,3-Dimethylbutane			16.9			
n-Hexane	58	0.3	3			
n-Heptane		18.8				
Other heptane isomers		77				
Methylcyclopentane	20					
2-Methylpentane			48.5			
3-Methylpentane	22		18.5			
n-Octane		3				
n-Pentane						9.0
Toluene		0.1				

[a]Composition in Liq. Vol. %.

TABLE 2
Physical Properties of Selected Hydrocarbon Solvents

	Types of solvent					
Properties	Hexane	Heptane	Isohexane	Neohexane	Cyclohexane	Cyclopentane
Boiling range						
°C	67–69	91–100	55–61	49–51	80–81	49–56
(°F)	(152–156)	(195–212)	(131–142)	(121–124)	(176–178)	(120–133)
Heat of vaporization						
cal/g	80	75.6	77	72.9	85.4	93
(Btu/lb)	(143.9)	(136)	(139)	(131.2)	(153.7)	(167)
Liquid specific heat						
cal/g/°C	0.533	0.528	0.52	0.516	0.433	0.422
Vapor specific heat						
cal/g/°C	0.386	0.385	0.39	0.382	0.29	0.271
Specific gravity						
(16°C/60°F)	0.679	0.694	0.66	0.655	0.781	0.738

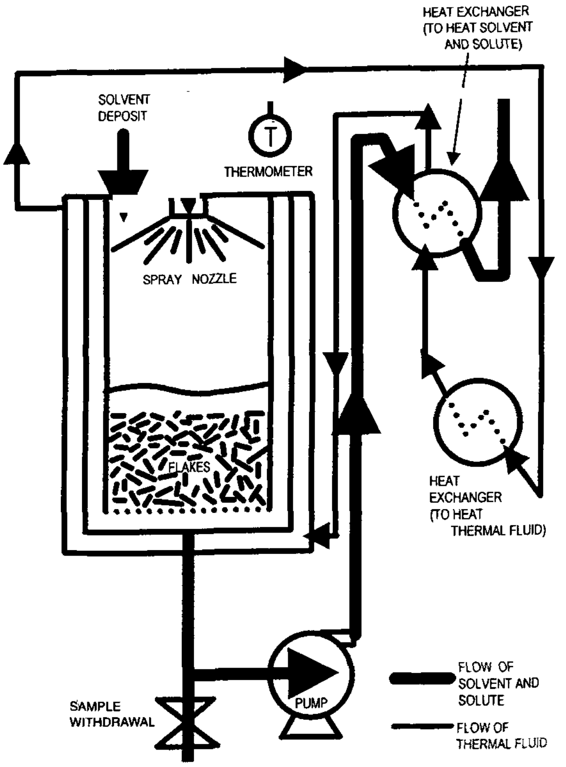

FIG. 1. Schematic of bench-scale single-stage extractor.

seed flakes were used for each test; (iii) a solvent-to-flakes ratio of 5.5 to 1 ensured a flooding condition of the flakes throughout the extraction; (iv) a miscella recycle flow rate of 36 mL/min/sq cm (9 gal/min/sq ft); (v) various starting miscella concentrations from 0 to 30% (w/w) were created by blending refined, bleached, and deodorized cottonseed oil obtained form a local grocery store with each solvent; (vi) starting miscella was recycled through the empty extractor until the desired extraction temperature was achieved; (vii) the basket of flakes was then placed quickly into the extracting chamber with the recycle pump stopped; (viii) extraction timer was started and recycle pump restarted; and (ix) a 10-mL miscella sample was taken at 2, 4, 6, 10, and 20 min of extraction to determine the amount of oil extracted from the flakes. The oil concentration increase in the miscella stream was determined by a weight difference method using a vacuum oven. Miscella concentration, which is expressed in percent of oil by weight, increases with extraction time and was corrected for solvent evaporation loss and oil disappearance through sampling.

Desolventization of several 50% miscellas, which were blends of equal weights of crude cottonseed oil and solvent, was accomplished as described in Table 3. The weight of reclaimed solvent was monitored using a Mettler balance. Free fatty acid, gossypol, and phosphorus content in the extracted crude oils were determined by AOCS Official Methods Ca 5a-40, Ca 13-56, and Ca 12b-92, respectively (10). Extracted cottonseed oils were refined in a 60% miscella at room temperature. An amount of alkali according to AOCS Method Ca 9e-52 (10) was added to the miscella. After 2 min high shear mixing with an Ultra-Turrax T25 (Janke & Kunkel GmbH & Co., Staufen, Germany), the mixture was kept at ambient conditions overnight, and refined oil was recovered by centrifugation with Dynac II Centrifuge (Becton, Dickinson & Co., Parsippany, NJ) for 20 min followed by decantation and desolventization in a rotary vacuum evaporator. Color of refined oils was measured by an automated colorimeter, Colourscan (The Tintometer, Ltd., Salisbury, England) with a 10-mm cell (11).

RESULTS AND DISCUSSION

Six replicate samples of cottonseed flakes were extracted by each of the six hydrocarbon solvents at their corresponding boiling points using the Soxtec procedure. The mean values of oil extracted and standard deviation were: hexane, 31.12% ± 0.57%; heptane, 31.67% ± 0.39%; cyclohexane, 29.96% ± 0.36%; cyclopentane, 28.76% ± 0.46%; isohexane, 27.89% ± 0.75%; and neohexane, 27.87% ± 0.52%. The normal paraffins were most efficient and significantly better than either cyclo or branched paraffins at 95% confidence level. Cyclohexane extracted 95.4% as much oil as the normal paraffins and significantly better than the remaining three solvents, cyclopentane, isohexane, and neohexane which were 91.6, 88.8, and 88.8%, respectively, effective as normal paraffins. The Soxtec procedure is similar to the Soxhlet procedure used by Ayers and Dooley (7). Soxtec results, however, showed that

TABLE 3
Extraction Characteristics of Hydrocarbon Solvents[a]

Solvent	Extraction temperature		Initial miscella concentration = 0%		Initial miscella concentration = 30%	
	°C	°F	E_i, % of oil extracted	E_c, % of oil extracted	E_i, % of oil extracted	E_c, % of oil extracted
Hexane	55	131	94.1	100.0	66.6	94.6
Heptane-75	75	167	90.5	100.2	57.0	77.9
Heptane-55	55	131	85.5	95.9	48.4	66.4
Isohexane	45	113	80.0	93.1	60.1	70.1
Neohexane	35	95	72.2	89.6	47.7	63.3
Cyclopentane	35	95	78.3	93.3	57.0	65.9
Cyclohexane	55	131	70.9	89.4	50.5	63.3

[a] E_i = Initial extraction rate at 2 min of extraction in percent of extractable oil from cottonseed flakes. E_c = Extraction capacity after 10 min of extraction in percent of extractable oil from cottonseed flakes.

normal paraffins were better solvents for cottonseed oil extraction than isohexane as reported by Ayers and Dooley (7).

In commercial practice, the solvent extraction temperature is usually 5.6°C (10°F) below the boiling point of a solvent. To mimic a single-stage commercial extraction, the following bench-scale extraction temperatures were selected for the six hydrocarbon solvents; hexane, 55°C; heptane, 55°C and 75°C; isohexane, 45°C; neohexane, 35°C; cyclohexane, 55°C; and cyclopentane, 35°C. Samples of miscella were taken at 2, 4, 6, 10, and 20 min from each extraction test and analyzed for oil concentration. This sampling scheme allowed the extraction results to be obtained in the form of a series of cumulative extraction curves (Fig. 2). It is interesting to note that hexane is very efficient in extracting oil out of cottonseed flakes, and in most tests, a steady-state miscella concentration was reached after 6 min. These extraction data permitted the calculation of the amount of oil extracted at a given time under the selected extraction conditions.

To facilitate further discussion of the extraction characteristics of these hydrocarbon solvents, the following two terms were selected: initial extraction rate (R_i) and extraction capacity (E_c). R_i is defined as the percent of oil extracted after 2 min. E_c is the percent of oil extracted after 10 min. The percent of oil extracted was calculated based on the total extractable oil from cottonseed flakes achieved by using normal hydrocarbons as 100%. With the bench-scale extractor, the first sample which could be effectively collected was 2 min after the extraction started. As indicated in Figure 2, R_i can be used to estimate solvent efficiency. In a commercial countercurrent extractor, the extraction zone is divided into four extraction sections plus one wetting section of full-fat flakes with the most concentrated miscella, and one final rinsing section of extracted flakes with fresh solvent. Each extraction section has a residence time of 7–10 min as the cottonseed flakes continuously move toward incoming fresh solvent. Therefore, E_c is a good measure for solvent effectiveness.

Full miscella in a commercial operation usually contains 20 to 30% crude oil. To assess the effect of miscella concentration on R_i and E_c, a series of preblended miscellas containing 5 to 30% oil, with a 5% increment, was used to extract cottonseed flakes. A plot of R_i vs. miscella concentration as well as E_c vs. miscella concentration for hexane at 55°C and heptane at 75°C (heptane-75) and 55°C (heptane-55) are shown in Figures 3 and 4, respectively. From these results, it is obvious that miscella concentration affects both R_i and E_c. Hexane is a very efficient solvent; its extraction rate and capacity did not decrease appreciably until miscella concentration exceeded 20%. For heptane, both R_i and E_c started declining after miscella concentration exceeded 10%. Improved solvency with increasing miscella concentration as reported by Kulkarni *et al.* (12) was not observed under the current experimental conditions. At 75°C, heptane is 5–10% less efficient and effective than hexane. But at 55°C, the differences in R_i and E_c for the two solvents increased to 20–30% when the miscella concentration exceeded 10%.

To aid in comparing the effectiveness of the five candidate hydrocarbon solvents with hexane for cottonseed extraction, the data of R_i and E_c at both 0 and 30% oil concentration in

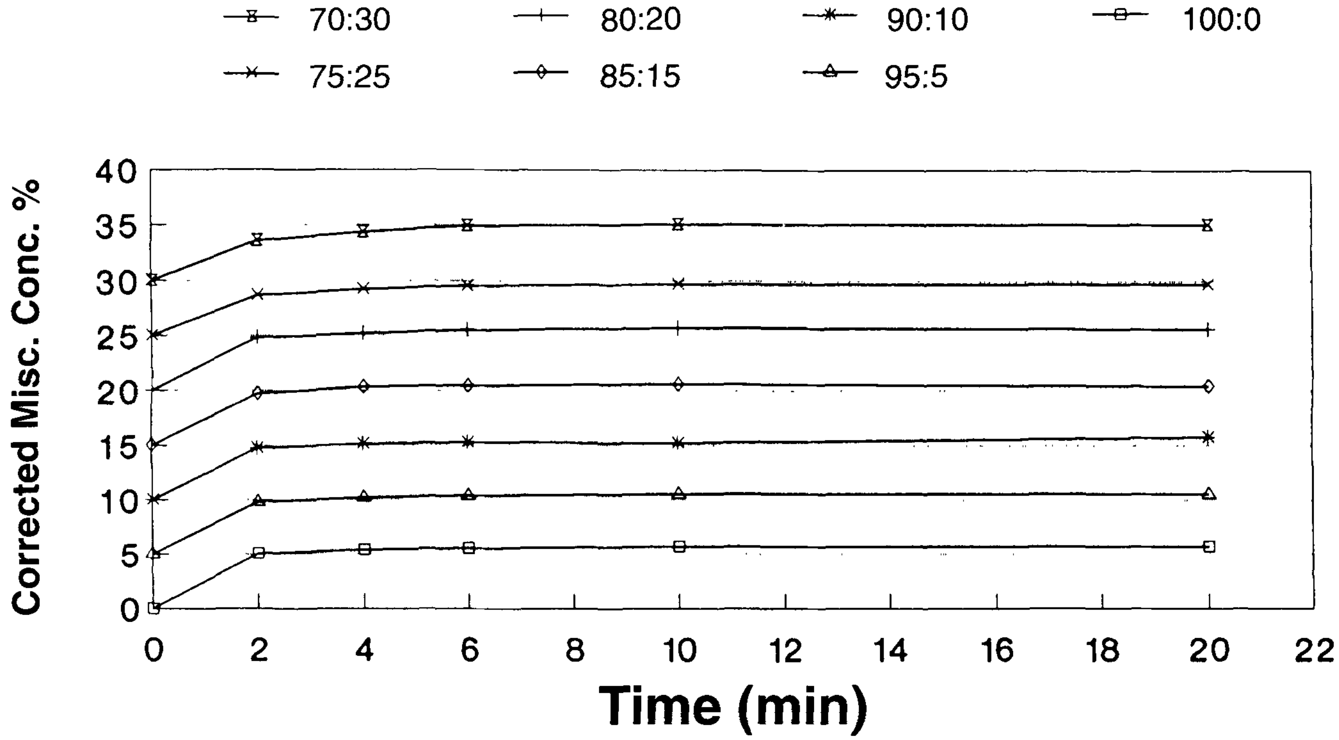

FIG. 2. Extraction data of hexane and hexane miscella with cottonseed flakes at 55°C.

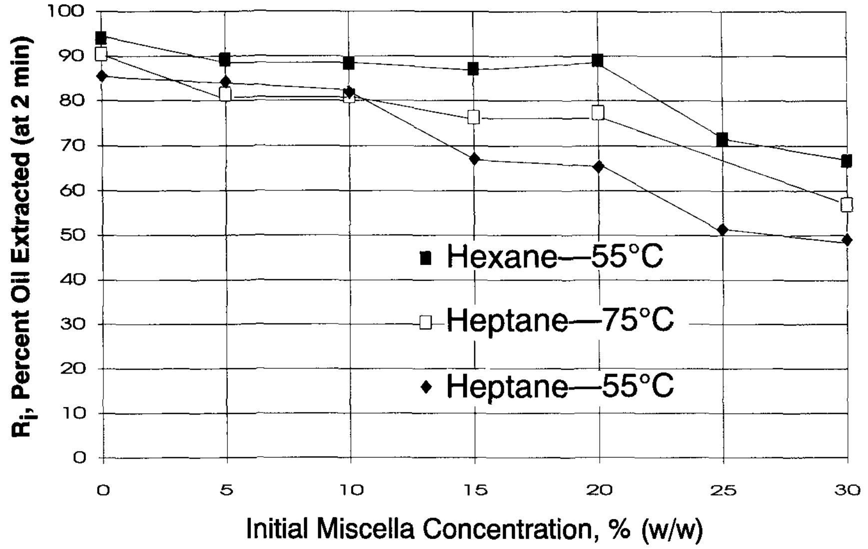

FIG. 3. Effect of initial miscella concentration on extraction rate at 2 min of extraction; R_i, initial extraction rate.

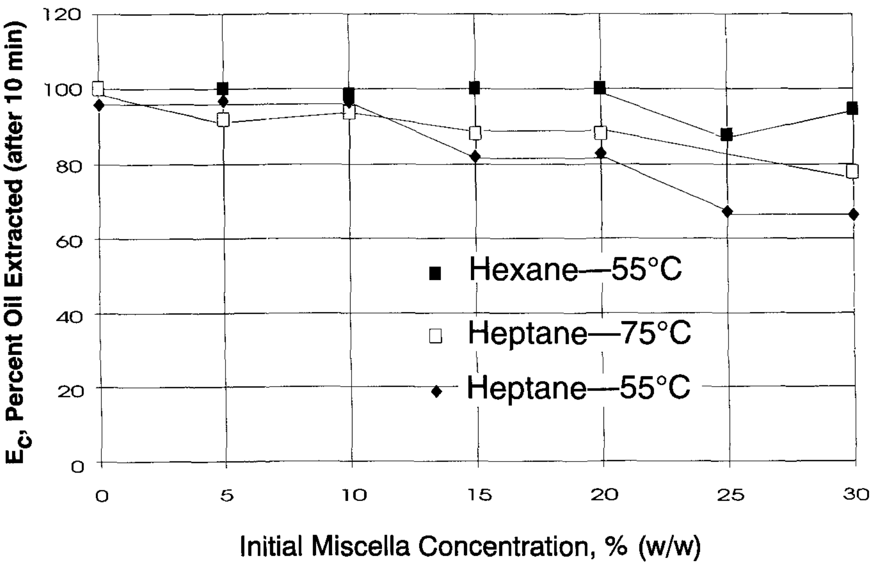

FIG. 4. Effect of initial miscella concentration on extraction capacity (E_c) after 10 min of extraction.

miscella for all solvents tested are presented in Table 3. For fresh solvents, i.e., 0% oil concentration, there were no statistical differences ($P < 0.05$) among hexane, heptane-75, heptane-55, and isohexane in their R_i's. Cyclo-paraffins were significantly less efficient ($P < 0.05$) with lower R_i values than hexane and heptane-75. R_i's for all six hydrocarbon solvents were drastically reduced by 20% to more than 30% as the oil concentration in the miscella reached 30%.

After continuous extraction for 10 min, the amount of oil extracted, i.e., E_c, by fresh solvents for all six hydrocarbon solvents was reasonably good. Their E_c values ranged from 90–100% oil extracted. However, the E_c for all five candidate solvents dropped more than 20% when miscella concentration reached 30%. Again it demonstrated that the candidate solvents were less effective than hexane, i.e., they did not have as good an E_c as did hexane. But all five candidate solvents have an E_c >90% at 0% miscella concentration, and an E_c >60% at 30% miscella concentration. This should be more than adequate to remove 99%+ oil from flakes under a countercurrent extraction and dilution process. The extraction time of 10 min per stage is apparently enough residence time for all candidate solvents to extract oil from cottonseed flakes. In commercial operation for either shallow or deep-bed extractor, the residence time for each extraction stage varies from

TABLE 4
Desolventization Conditions

	Hexane	Heptane	Isohexane
Initial stage			
Miscella (%)	50	50	50
Bath temperature (°C)	65	93	55
Vacuum, mm Hg	380	380	380
(in Hg)	(15)	(15)	(15)
Duration (min)	28	28	12
Second stage			
Bath temperature (°C)	95	97	97
Vacuum, mm Hg	125	125	125
(in Hg)	(25)	(25)	(25)
Duration (min)	52	32	68
Residual solvent (%)	2.89	4.84	1.34
Condenser (°C)	2	2	-2

7–10 min or an average of 45 min for the entire extraction process.

Desolventization of 50% oil in miscella for hexane, heptane, and isohexane was conducted with a rotary vacuum evaporator under the condition described in Table 4; the results are shown in Figure 5. As expected, due to the lower boiling point of isohexane, it is much easier to remove isohexane than hexane. However, isohexane may require a more efficient condenser to recover than hexane. The desolventization characteristic of heptane is similar to that of hexane.

Most of the candidate solvents have a comparable liquid phase-specific heat, as shown in Table 2. Therefore, major differences in energy requirements to recover the solvents will be determined by their corresponding heats of vaporization and boiling points. Heptane, due to higher boiling, and two cyclo-paraffins, due to higher heat of vaporizations, are expected to demand more energy or steam to recover than hexane. Assuming miscella or extracted flakes are desolventized from near-extraction temperature, and no energy loss to the surroundings, total energy required to recover one gram of hexane from 20% miscella is estimated to be 89.3 calories. Heptane, cyclopentane, and cyclohexane require 17.9, 16.5 and 11.4% more energy, respectively, than hexane, while isohexane and neohexane need 2.2 and 6.2% less energy, respectively, than hexane to recover.

The product quality produced by each of the candidate solvents is as important as the solvent efficiency. Free fatty acid, gossypol, and phosphorus content in crude oil will affect oil quality in terms of refining loss and refined color. Relatively consistent free fatty acid levels for crude oils derived from all six solvents, as shown in Table 5, implied that the quality of flakes was relatively constant during the entire period of experiment. Phosphorus content in the crude oils indicated a slightly increased solubility of phospholipids in normal paraffins and in higher extraction temperatures. While normal and branched paraffins demonstrated comparable extractability of gossypol from cottonseed flakes, cyclo-paraffins removed much more—almost twice the amount—of gossypol than either normal or branched paraffins. Bench-scale refining of these crude oils by a miscella refining procedure showed no

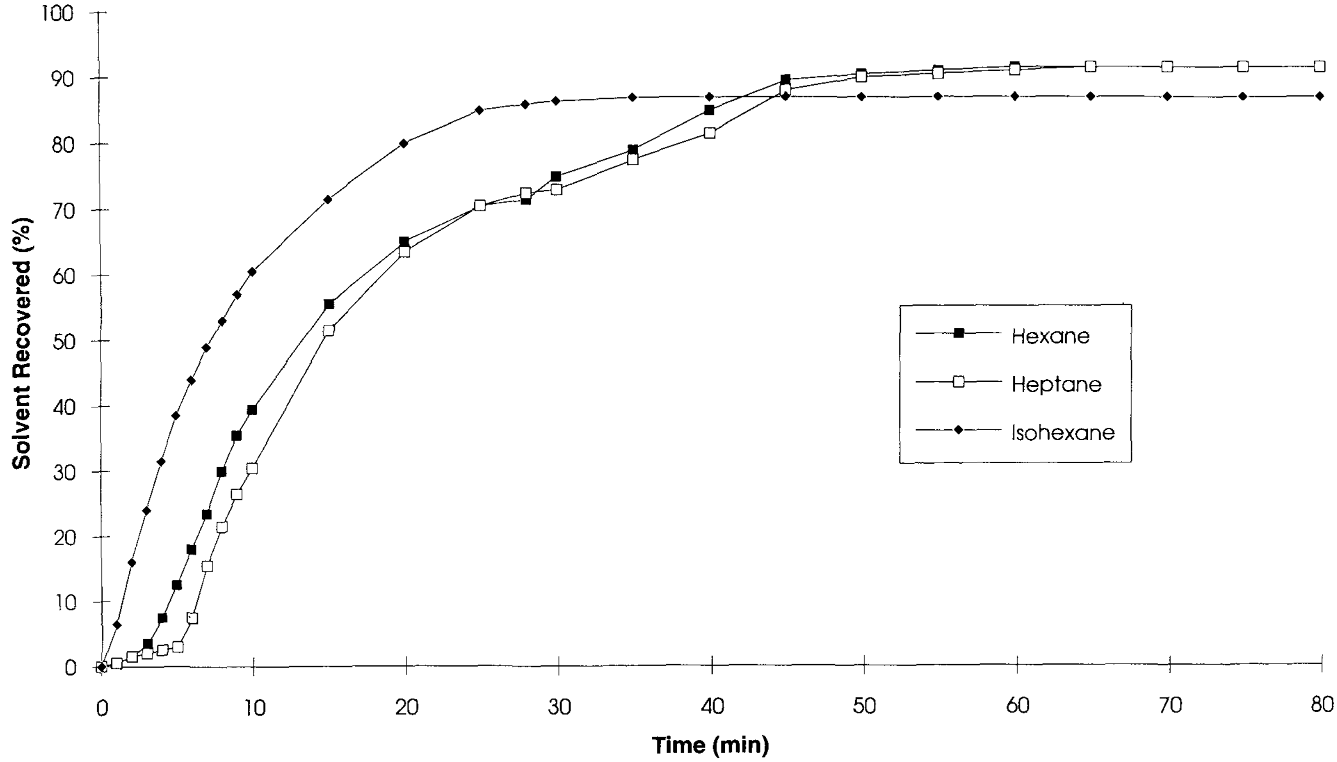

FIG. 5. Desolventization characteristics of hexane, heptane, and isohexane at 50% miscella concentration.

TABLE 5
Properties of Extracted Cottonseed Oils

Solvent	Free fatty acid (%)	Gossypol (%)	Phosphorus (ppm)	Crude color red (10 mm)	Refined color red (10 mm)
Hexane	2.4	0.34	515	12.0	0.7
Heptane	2.4	0.23	593	11.4	0.7
Isohexane	2.8	0.29	427	16.4	0.8
Neohexane	2.5	0.16	394	8.8	0.6
Cyclopentane	2.8	0.54	478	20.5	0.7
Cyclohexane	2.8	0.64	401	19.6	0.8

significant color differences as measured by the Colourscan.

Based on the bench-scale extraction results, on extraction capacity, E_c, and initial extraction rate, R_i, all five candidate solvents, although not as good as hexane, can adequately extract cottonseed flakes. After reviewing the availability and cost of these five candidate solvents and the preferred operating temperature range which is close to that of hexane, it became obvious that heptane and isohexane are the most likely alternate hydrocarbons to replace hexane. The next step is to conduct either pilot-scale evaluation or plant trials to compare the performance of heptane and isohexane vs. hexane. Results derived from plant trials will allow a better assessment of cost effectiveness of these two recommended alternative solvents.

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REFERENCES

1. Hron, Sr., R.J., M.S. Kuk, G. Abraham and P.J. Wan, *J. Am. Oil Chem. Soc. 71*:417 (1994).
2. Lusas, E.W., L.R. Watkins and K.C. Rhee, *Edible Fats and Oils Processing: Basic Principles and Modern Practices*, edited by D.R. Erickson, American Oil Chemists' Society, Champaign, 1990, p. 56.
3. Wakelyn, P.J., and L.A. Forster, Jr., *Oil Mill Gazetteer*, June:21 (1994).
4. Wakelyn, P.J., *Cotton Gin and Oil Mill Press*, July 27:12 (1991).
5. Hron, R.J., Sr., S.P. Koltun and A.V. Graci, Jr., *J. Am. Oil Chem. Soc. 59*:674A (1982).
6. Johnson, L.A., and E.W. Lusas, *Ibid. 60*:181A (1983).
7. Ayers, A.L., and J.J. Dooley, *Ibid. 25*:372 (1948).
8. Spender, P.S., *Advances in Modern Environmental Toxicology, Vol. VI, Applied Toxicology of Petroleum Hydrocarbons*, edited by H.N. MacFarland, C.E. Holdsworth, J.A. MacGregor, R.W. Call and M.L. Lane, Princeton Scientific Publishers, Inc., Princeton, 1984, pp. 199–214.
9. Abraham, G., R.J. Hron and S.P. Koltun, *Ibid. 65*:129 (1988).
10. *The Official Methods and Recommended Practices of the American Oil Chemists' Society*, 4th edn., American Oil Chemists' Society, Champaign, 1993.
11. Wan, P.J., and D.R. Pakainen, *J. Am. Oil Chem. Soc. 72*:455 (1995).
12. Kulkarni, B.S., E.L. D'Aquin and A.V. Graci, Jr., *Ibid. 32*:691 (1955).

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