Alternative Hydrocarbon Solvents for Cottonseed Extraction: Plant Trials

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ABSTRACT: Hexane has been used for decades to extract oil from cottonseed and is still the solvent of choice for the edible-oil industry. Due to increased regulations as a result of the 1990 Clean Air Act and potential health risks, the edible-oil extraction industry urgently needs an alternate hydrocarbon solvent to replace hexane. Based on laboratory-scale extraction tests, two hydrocarbon solvents, heptane and isohexane, were recommended as potential replacements for hexane. A cottonseed processing mill with a 270 MT/day (300 tons/day) capacity agreed to test both solvents with their expander–solvent process. Extraction efficiencies of isohexane and heptane, judged by extraction time and residual oil in meal, refined and bleached color of miscella refined oil, and solvent loss, were comparable to that of hexane. However, fewer problems were encountered with the lower-boiling isohexane than with the higher-boiling heptane. With isohexane, the daily throughput increased more than 20%, and natural gas consumption decreased more than 40% as compared to hexane.

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KEY WORDS: Alternative solvents, cottonseed, expander–solvent, extraction, heptane, hexane, isohexane, miscella, miscella refining.

It is anticipated that states will soon regulate the emission of volatile organic compounds (VOC) and hazardous air pollutants (HAP) more stringently because of the 1990 Clean Air Act (CAA) (1,2). Hexane, the extraction solvent for cottonseed and many other oilseeds, will likely be regulated as both a criteria pollutant and an HAP. Criteria pollutants include particulate matter, ozone or its precursors, such as VOC. The main component of commercial hexane, *n*-hexane, is one of the 189 HAP listed in the CAA (2). The emission limit for a criteria pollutant is 100 tons per year (tpy) per plant, and for an HAP it is 10 tpy. Exceeding either limit will require a Federal Operating Permit and an annual fee, based on annual tons of hexane consumed (1).

While the industry continues its effort to reduce the loss of hexane, laboratory research of alternative hydrocarbon solvents with less health risk led to a study of two candidate solvents, heptane and isohexane (3). Performance trials of both solvents and of hexane were conducted in a cottonseed processing facility in March 1994. Results of these trials are reported.

EXPERIMENTAL PROCEDURES

Seven thousand gallons of heptane and of isohexane were supplied by Phillips Petroleum Company (Bartlesville, OK). Chemical compositions and some selected physical properties for hexane, heptane, and isohexane, as provided by the supplier, are listed in Tables 1 and 2, respectively.

Both candidate solvents were evaluated in a cottonseed expander–solvent extraction mill (4) designed to crush 250 MT/day (275 tons/day), but operated at 270 MT/day (300 tons/day). This mill does miscella refining. A flow diagram of the operation is shown in Figure 1. When isohexane was used, an additional cooling step, Cooler II, was added to ensure that the temperature of collets remained below 37.8°C (100°F) before entering the extractor. Operating conditions were recorded for the two candidate solvents as well as for hexane.

Residual oil content of extracted collets and meals was

TABLE 1
Composition of Solvents Used in Plant Trials[a]

Component	Hexane (Lv%)[b]	Heptane (wt%)	Isohexane (wt%)
Hydrocarbon with 5C or less			0.9
2,2-Dimethylbutane		0.1	14.0
2,3-Dimethylbutane		0.1	15.9
2-Methylpentane	0.2	0.2	46.3
3-Methylpentane	4.0	0.1	20.1
n-Hexane	86.2		2.6
Methylcyclopentane	9.6		0.2
Cyclopentane derivatives		7.1	
Cyclohexane derivatives		0.8	
2-Methylhexane		21.6	
3-Methylhexane		28.2	
n-Heptane		23.6	
Other isoheptanes		12.6	
Toluene		3.5	
Other unsaturated hydrocarbons		2.1	

[a] Data were provided by the supplier.
[b] Lv% = Liquid volume %.

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TABLE 2
Physical Properties of Selected Hydrocarbon Solvents[a]

Properties	Types of solvent Hexane	 Heptane	 Isohexane
Boiling range			
°C	67–69	91–100	55–61
(°F)	(152–156)	(195–212)	(131–142)
Flash point			
°C	–29	–9	–29
(°F)	(–20)	(15)	(–20)
Heat of vaporization			
cal/g	80	75.6	77
(Btu/lb)	(143.9)	(136)	(139)
Liquid specific heat			
cal/g/°C	0.533	0.528	0.52
Vapor specific heat			
cal/g/°C	0.386	0.385	0.39
Specific gravity			
(16°C/60°CF)	0.679	0.694	0.66

[a]Data provided by the supplier of (Phillips Petroleum Co., Bartlesville, OK).

monitored at least once every eight hours by the plant laboratory. Free fatty acid, gossypol, and phosphorus content in the extracted crude oils were determined at the Southern Regional Research Center (SRRC) and a commercial laboratory according to AOCS Official Methods Ca 5a-40, Ca 13-56, and Ca 12b-92 (5), respectively. Refined oil was bleached in a commercial laboratory, and the color of refined and bleached oil was measured according to AOCS Method Cc 13b-45 (5) or with an automated colorimeter, Colourscan (Tintometer Model AF960; Salisbury, England) (6). Miscella concentration, expressed as percent oil by weight in the miscella (mixture of oil and solvent), was estimated by a density method at the mill.

RESULTS AND DISCUSSION

Some of the extraction conditions and results for hexane, isohexane, and heptane are shown in Table 3. When the residence time of collets in the extractor, full miscella concentration, and residual oil in the extracted collets were compared, both candidate solvents showed an extraction efficiency comparable to that of hexane. Results obtained from a separate week-long plant trial showed that the residual oil in extracted collets was 1.00 ± 0.17% for isohexane (mean ± standard deviation of 16 samples) and 0.87 ± 0.06% for hexane (20 samples). These additional plant results confirmed the laboratory–scale observation (3) that isohexane can extract >97% oil out of cottonseed and that hexane is slightly more efficient than isohexane under the extraction conditions described in Table 3. Only occasional, slightly higher pressure was noted in the extractor for isohexane, which was believed to be caused by insufficient cooling of the collets prior to extraction.

High energy demand to recover heptane from marc (extracted collets) slowed the entire process. For this solvent, residence time in the extractor, in some cases, was extended to more than 100 min as opposed to a normal residence time of 46 min. This extended extraction time yielded collets with lower residual oil (Table 3), but did not affect the oil quality (Table 4).

Plant refinery records and results for all three solvents (Table 4) demonstrated that oils derived from isohexane and heptane were bleachable to a color similar to that from hexane. The cloudy appearance observed in refined isohexane miscella was of initial concern and was believed to be caused by higher-than-optimum operating temperatures for the miscella refining process. However, the refined oil still met the bleach-

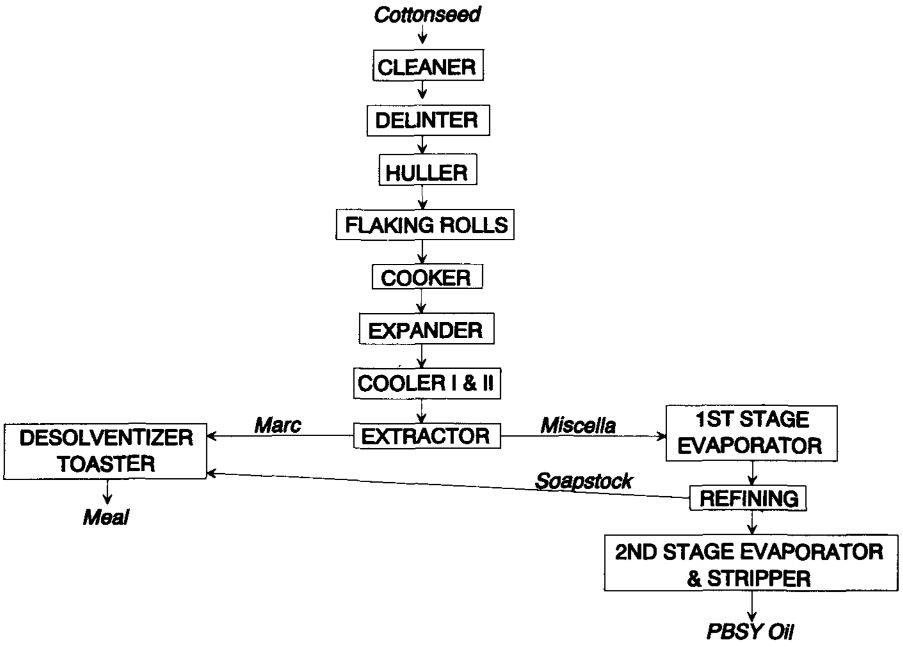

FIG. 1. Flow diagram for expander–solvent extraction of cottonseed.

TABLE 3
Extraction Performance[a]

Operation condition	Hexane	Isohexane	Heptane
Collet temp. to extractor			
°C	65.6	48.8	70.3
(°F)	(150)	(119.8)	(158.6)
Extractor temp.			
°C	63.5	57.9	65.9
(°F)	(146.3)	(136.2)	(150.6)
Residence time in extractor, min	45.0	46.2	91.4
Concentration of full miscella, %	29.5	31.1	29.9
Residual oil in extracted collets, %	0.93	1.00	0.66
Average moisture, %	11.3	10.9	10.5
Desolventizer toaster temp.			
°C[b]	60–99	54–107	68–107
(°F)	(140–210)	(130–225)	(154–225)

[a] All values were supplied by the plant.
[b] The temperature (temp.) range reflects the various functions of the five rings in each desolventizer/toaster.

TABLE 4
Refinery Operation Conditions and Results[a]

Operation condition	Hexane	Isohexane	Heptane
Second stage evaporator temp.			
°C	120.8	133.5	150.6
(°F)	(249.4)	(272.3)	(303.1)
Stripper–vacuum, mm Hg	23.5	21.2	24.2
Stripper–bottom temp.			
°C	122.2	122.8	134.6
(°F)	(251.9)	(253.1)	(274.4)
Miscella concentration before refining, %	67.0	67.0	66.6
Miscella free fatty acid, %	1.59	1.68	1.54
Miscella refined oil color, red	4.0	4.2	4.1
Bleached color, red	1.6	1.5	1.6

[a] All values were supplied by the plant; temp., temperature.

TABLE 5
Daily Throughput Rate and Solvent Consumption

Operation condition	Hexane	Isohexane	Heptane
Throughput rate			
Metric tons CS/day	272	290–332	256
Tons CS/day	300	320–366	282
As % of hexane	100	107–122	67–77
Solvent consumption			
As % of hexane	100[a]	97.4[b]	112.6[c]

[a] Annualized average solvent consumption. CS, cottonseed.
[b] Weekly average solvent consumption.
[c] Average of three-day operation.

able color standard for Prime Bleachable Summer Yellow (PBSY), <2.5 red (7). Miscella free fatty acid contents before refining were comparable for all three solvents.

Desolventization of isohexane-extracted collets acid operated smoothly. Due to the lower boiling range of isohexane, throughput rate of the desolventizer/toaster (D/T) was 10–20% higher than that of hexane. The higher-boiling heptane raised the D/T energy load and forced a 20–30% reduction in daily throughput (Table 5). The experiment with heptane was stopped after three days of operation because of the loss in throughput. In addition, the solvent loss of heptane was 12% higher than that of hexane's annualized average loss. Losses of isohexane, on the other hand, were about 86.8 to 97.4% of hexane. However, due to the short duration of the plant test (isohexane, one week; heptane, three days), the solvent loss data may not reflect accurate differences between the solvents.

Two-day samples of miscella before refining (MBR) and miscella refined oil (MRO) were obtained from hexane, isohexane, and heptane extractions. MBR samples were desolventized in a rotary vacuum evaporator at SRRC. Compositional analysis and color readings of oils derived from MBR and MRO were done; their mean values are presented in Table 6. Oils of MBR samples derived from heptane contained less gossypol and more phosphorus than those derived from hexane and isohexane, which confirmed the bench extraction results (3). This implied that heptane has greater solubility of phospholipids and less affinity toward gossypol than the other two hydrocarbon solvents. Color of desolventized MBR or crude oils varied proportionally to the amount of gossypol present. All MRO samples were desolventized in the mill operation and were sufficiently low in moisture and volatiles, phosphorus content, and light in color. MRO samples derived from isohexane miscella contained more than 20 ppm phosphorus, which is significantly higher than that from hexane or heptane. This problem could be caused by refining at higher-than-optimum temperatures and should be verified and corrected during a proposed extended run. All MRO oils produced from the three solvents were bleached by a commercial laboratory to a color less than the required 2.5 red for PBSY, which confirmed the plant results shown in Table 4. Composition of meals produced from all three solvents (Table 7) indicated some consistency. Oil contents of meals are higher than of extracted collets (Table 3), due to the addition of soapstock from the refining process. The differences in protein contents were likely caused by variation in the amount of hulls present in dehulled meat fractions.

From the standpoint of process performance and quality of products, it appears that isohexane can be used to replace hexane with minimum retrofit. Heptane would require greater D/T capacity to maintain the same tonnage throughput found with hexane. This might not be economical for most edible-oil extraction operations, as D/T capacity often limits throughput. However, the high boiling point of heptane allows it to be operated at a broad temperature range, from ambient to 80°C (176°F), which could be advantageous in extracting substances with melting points higher than vegetable oils. Isohexane boils at 55°C (131°F) and therefore has a rather narrow operating temperature range, between ambient and the 45°C extraction temperature. This lower extraction temperature may also affect the extraction efficiency of iso-

TABLE 6

Composition and Color of Oils from Miscella Before Refining (MBR) and Miscella Refined Oil (MRO)[a]

	Hexane		Isohexane		Heptane	
Analysis	MBR	MRO	MBR	MRO	MBR	MRO
Moist and volatile (%)	0.35	0.04	0.85	0.05	1.50	0.04
Free fatty acid (%)[b]	1.95		2.40		1.75	
Gossypol (%)	0.738		0.697		0.466	
Phosphorus (ppm)	737	3.0	707	23.5	778	3.5
Color (red)[c]	12.5	3.8	10.3	4.9	8.8	3.7
Bleached color (red)		1.3		1.9		1.1

[a] All values are averages of duplicate samples.

[b] Free fatty acid in MBR was done at Southern Regional Research Center (SRRC) New Orleans, LA on samples collected from plant.

[c] Color of oil derived from MBR was read in a 5-mm cell, and color of MRO was read in a 133.35-mm (5.25-in) cell with an automated Colourscan (6).

TABLE 7

Composition of Meals[a]

Composition	Hexane	Isohexane	Heptane
Moisture (%)	10.7	9.7	8.2
Oil (%)	2.4	2.3	2.7
Protein (%)[b]	41.9	44.4	39.8

[a] Average of two or more replicate samples.

[b] Protein % = (nitrogen %) × 6.25.

TABLE 8

Natural Gas Usage for Steam Generation[a]

Solvent	CS processed per week (MT)	Gas usage per week (L)	% Savings (per MT CS)	% Savings (per week)
Isohexane	1,872.5 (2,064 tons)	184,071 (202.9 MCF)	38.3	42.8
Hexane	2019.4 (2,226 tons)	321,602 (354.5 MCF)	Control	Control

[a] MCF = 1000 cubic feet. See Table 5 for other abbreviation; MT, metric ton.

hexane, as indicated by slightly higher residual oil in spent collets (Table 3) than in hexane. Overcoming the slightly reduced extraction efficiency of isohexane is believed achievable by some process adjustments.

The main advantage of using isohexane, aside from its relatively lower health risk (8), is the lower energy required for its recovery. Table 8 shows an example of the energy savings, based on natural gas consumption for steam generation for a one-week trial run. Isohexane reduced plant natural gas consumption by more than 40% over hexane operation, as opposed to a theoretical estimate of less than 3% savings (3). This large energy savings could be due to the unique operation conditions of the D/T at this plant. Currently, we are working to understand the reasons for these savings. Rapid removal or stripping of isohexane should also provide the basis for a dramatic increase in throughput as was observed during this plant trial.

Isohexane will always be slightly more expensive than hexane, due to the additional isomerization process for its production. However, the improved throughput and the reduced energy requirement for isohexane should compensate for the solvent cost differential, particularly for mills operating near or above designed capacity. Thus under present economic, environmental, and regulatory concerns, isohexane is a viable choice to replace hexane for cottonseed extraction. In addition, the lower-boiling range of isohexane would offer the benefit of minimizing heat-induced oil quality problems. We anticipate that a similar conclusion could be arrived at for other oilseed extraction industries.

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