# Cottonseed Extraction with a New Solvent System: Isohexane and Alcohol Mixtures

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**ABSTRACT:** A solvent system, consisting of isohexane and 5 to 25% alcohol, either ethanol (EtOH) or isopropyl alcohol (IPA), was tested for extracting gossypol and oil from cottonseed. The test results indicate that this new solvent system not only is effective in removing free and total gossypol but also is as efficient as *n*-hexane when extracting oil. The amino acid analysis of cottonseed meal, produced by the new solvent system, is similar to that produced by commercial *n*-hexane. Present commercial cottonseed extraction and downstream processing of cottonseed oil refining may need little change to adopt this new solvent system. This new solvent system may lead to a solution to the gossypol problem of cottonseed extraction.

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**KEY WORDS:** Cottonseed, extraction, free gossypol, meal, new solvent, oil, total gossypol.

Because of the 1990 Clean Air Act (CAA) and potential health risks, an alternative solvent or solvent system may eventually replace hexane as the extraction agent of vegetable oil. The main component of commercial hexane, *n*-hexane, is listed as a hazardous air pollutant in the CAA (1). The recently tested alternative solvents include isohexane, ethanol (EtOH), and isopropyl alcohol (IPA). These alternative solvents are of interest for the following reasons: (i) isohexane is considered to be environmentally less harmful (2), and (ii) ethanol and IPA have potential to remove toxic, carcinogenic, and antinutritional factors, thereby improving the quality of extracted meal for food and feed products and increasing its economic value. By using isohexane, the industry and the consumer may benefit from reduced processing costs, decreased energy usage, and fewer environmental hazards (2). Benefits of utilizing ethanol or IPA include enhancement of food and feed safety, reducing fire and explosion potential, and expansion of markets for cottonseed meal because of enhanced product quality. The industry has long sought to achieve simultaneously the two main goals through a single extraction agent, but so far no success has been reported. Numerous technical investigations of cottonseed extraction by ethanol (3–8) and IPA (9,10) have been reported; however, the key drawback of alcohol-based solvent extraction was attributed to the limited solvent power of alcohol compared with hexane, eventually resulting in an increased process cost (11). Although there were a few attempts to extract cottonseed with solvent systems of *n*-hexane and alcohols (12,13), isohexane and other hydrocarbons, such as benzene, cyclohexane and *n*-hexane (14), no prior documentation has been made of cottonseed extraction with solvent mixtures that consist of isohexane and alcohols.

To overcome the disadvantages of *n*-hexane, a solvent system of isohexane and either 5 to 25% ethanol or IPA was tested to extract cottonseed oil and gossypol.

## MATERIALS AND METHODS

Mill-run cottonseed raw flakes by a Mississippi oil mill (plant in Monroe, LA) from the harvest of the previous season were used for extraction. Flake thickness was 0.25 mm, and moisture was controlled to 9.5% before extraction. A modified AOCS Method Aa 4-38 (15) was used to produce crude oil and to establish the baseline data of *n*-hexane extraction: a Soxhlet extractor was used in place of a Butt-type, and petroleum ether was replaced by test mixtures. The same extraction was conducted with isohexane-based solvents to determine the efficacy of gossypol and oil extraction. *n*-Hexane (Baker Chemicals, Phillipsburg, NJ) of reagent grade and isohexane (Phillips Petroleum, Bartlesville, OK) of commercial

**TABLE 1**
**Composition of Commercial-Grade Isohexane Solvent and Boiling Point Ranges**[a]

| Component | Composition (wt%) | Boiling point °C (°F) |
|---|---|---|
| Cyclopentane | 0.25 | 71.8 (161.2) |
| Isopentane | 0.24 | 27.8 (82.1) |
| *n*-Pentane | 0.29 | 36.1 (97.0) |
| 2,2-Dimethylbutane | 9.87 | 49.7 (119.5) |
| 2,3-Dimethylbutane | 18.26 | 59.9 (140.0) |
| 3-Methylpentane | 18.57 | 63.2 (145.8) |
| 2-Methylpentane | 50.54 | 60.3 (140.5) |
| *n*-Hexane | 1.5 | 68.7 (155.6) |
| Methylcyclopentane | 0.1 | 71.8 (161.2) |

[a] Boiling point range of tested isohexane solvent (provided by Phillips Petroleum Company) by ASTM D-216: initial and final boiling point = 57.2/61.1°C (135/142°F).

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solvent grade (97+%) were used without further purification. The ASTM distillation boiling point (b.p.) and other physical properties of isohexane are given in Table 1. USP-grade ethanol (USI Chemicals, Cincinnati, OH) and IPA (Fisher Scientific, Fairlawn, NJ) were used as supplied. Crude oils were analyzed for color determination with a Colorscan (Tintometer Model AF960; Salisbury, United Kingdom), gossypol and free fatty acid by AOCS methods (15), phosphorus by induction-coupled plasma, and amino acid analysis of extracted meal by high-performance liquid chromatography (HPLC).

## RESULTS AND DISCUSSION

Extraction of vegetable oil essentially aims at recovery of triacylglycerols (TAG) from oil-bearing seeds. Because of the narrow variation in physicochemical characteristics of these TAG, mostly with carbon numbers between 48 and 54, it is not difficult to find a single extraction agent that can efficiently recover the cottonseed TAG. When recovery is limited to TAG, *n*-hexane is an excellent solvent for extracting TAG from a variety of oilseeds. However, in cottonseed extraction it is desirable to recover not only TAG but also gossypol. The extraction performance of a solvent is generally determined by the solubility characteristics between the extracting agent and the solute. The solubility characteristics are precisely represented by Hildebrand's (16) solubility parameter, defined as follows:

$$\delta = \left[(\Delta H - RT)/V^1\right]^{1/2} \qquad [1]$$

where $\Delta H$ represents heat of vaporization, $R$ = gas constant, and $V^1$ = molal volume of the extraction solvent. Because of the similarity of $\Delta H$ and $V^1$ values in the cottonseed TAG, isohexane behaves essentially equal to *n*-hexane in extracting cottonseed TAG. *n*-Hexane's value for $\delta$ at 25°C is 7.3. This value may also be used for isohexane in most practical applications. The solubility characteristics of gossypol differ from that of cottonseed TAG. The polarity, internal energy, and molar volume of solvent and their relationship with solutes determine the solubility characteristics. Cottonseed TAG are nonpolar components, whereas gossypol is polar. Because of this high polarity, gossypol is readily extracted by polar solvents, such as EtOH and IPA. Estimated $\delta$ values for EtOH and IPA at room temperature are 12.7 and 11.7, respectively. Because of the two different solubility characteristics between TAG and gossypol, it is nearly impossible to recover both types of cottonseed lipids by a one-step extraction operation with a single extracting agent, such as hexane or alcohol. A rational solution to this problem is to select a solvent mixture that consists of hexane and an alcohol. Fortunately, the new solvent system may be easily adapted to the present practice of cottonseed extraction.

Isohexane is a good choice for the base solvent, because *n*-hexane is considered to be a health risk (2). The amount of alcohol to be added to the base solvent determines the effectiveness of the solvent mixture for extracting gossypol. For the sake of simplicity, three alcohol concentrations were chosen for the test mixtures: 5, 10, and 25 vol% of EtOH or IPA added to isohexane. These concentrations amount to *ca.* 10, 20, and 43 mol%, respectively, for EtOH mixtures, and *ca.* 8, 17 and 37 mol% for IPA. The performance of oil and gossypol extraction by these solvent mixtures is presented in Table 2, which shows that the amount of lipid recovered by these solvent mixtures is invariant around 27 ± 1%. This is exactly equal to that extracted by 100% *n*-hexane. This result indicates that the addition of alcohols to isohexane has not affected the extraction capability of solvent mixtures for recovering TAG. However, these solvent mixtures definitely demonstrate the powerful capability of gossypol extraction. Extraction of total gossypol is generally harder than extracting free gossypol. The results in Table 2 indicate that an addition of only 5% alcohol, either EtOH or IPA, enabled the solvent mixture to reduce total gossypol by *ca.* 45%, whereas 70+% of free gossypol is removed. These reductions were compared to the gossypol that remained in the flakes after extraction with 100% isohexane. As shown in Table 3, the addition of 5 to 10% alcohol to isohexane does not substantially increase the b.p. or $\Delta H$ of the mixture.

The unfavorable process economics of 100% ethanol (11) extraction of cottonseed was due to the poor solubility of

**TABLE 2**
**Oil and Gossypol Extraction Performance by Hydrocarbon Solvent Mixtures with Alcohols**

| Base hydrocarbon (%) | Alcohol type (%) | Extraction oil yield[a] (%) | Gossypol Total[b] (%) | Gossypol Free[b] (%) |
|---|---|---|---|---|
| Isohexane, 100 | None | 26.2 | 1.30 | 0.95 |
| Isohexane, 95 | EtOH, 5 | 27.5 | 0.72 | 0.25 |
| Isohexane, 90 | EtOH, 10 | 26.7 | 0.41 | 0.18 |
| Isohexane, 75 | EtOH, 25 | 27.7 | 0.60 | 0.11 |
| Isohexane, 95 | IPA, 5 | 28.0 | 0.70 | 0.30 |
| Isohexane, 90 | IPA, 10 | 27.5 | 0.50 | 0.26 |
| Isohexane, 75 | IPA, 25 | 29.0 | 0.45 | 0.12 |
| *n*-Hexane, 100 | None | 27.0 | 1.10 | 1.05 |

[a] Arithmetic average with a variation of ±5% of the reported value.
[b] Gossypol in extracted flakes. Raw flakes contained 1.05% total and 1.03% free gossypol before extraction. IPA, isopropyl alcohol.

**TABLE 3**
**Range of Boiling Point (b.p.) of Isohexane/Alcohol Mixtures and Heat of Vaporization Increment ($\Delta H_v$) in Comparison to *n*-Hexane or Isohexane**

| Composition (vol%) Isohexane | Composition (vol%) Alcohol | Estimated b.p. range (°C) | $\Delta H_v$ % increment *n*-C6[a] | $\Delta H_v$ % increment Iso-C6[b] |
|---|---|---|---|---|
| 100 | 0 | 57/61 | — | — |
| 95 | EtOH | 57.5/61.5 | 4 | 8 |
| 90 | EtOH | 58.0/62.0 | 15 | 17 |
| 75 | EtOH | 60.5/64.5 | 35 | 40 |
| 95 | IPA | 57.5/61.5 | 3 | 6 |
| 90 | IPA | 58.5/62.5 | 9 | 13 |
| 75 | IPA | 61.0/65.0 | 26 | 32 |

[a] *n*-Hexane.
[b] Isohexane. For other abbreviation see Table 2.

TAG in alcohol, which required at least more than double the amount of alcohol solvent to achieve the same level of extraction with *n*-hexane. The prohibitive process economics was also attributed to the high value of latent heat for the alcohol.

Because of the similar solubility characteristics of the new solvent mixtures to *n*-hexane, and the minimal increment in the $\Delta H$ for the new solvents with 5 to 10% of EtOH or IPA, the process economics with the new solvent system is expected to be essentially equal to that of hexane. It is expected that the gossypol extraction performance shown in Table 2 can be improved further by using a multistaged extractor. In the 1970s, there was a report by Osman *et al.* (14) that isohexane extracted more gossypol from cottonseed meat than *n*-hexane. However, the recent report by Wan *et al.* (2) did not support the Osman *et al.* findings. The results shown in Table 2 are in agreement with the findings of Wan *et al.*.

Table 4 represents the crude oil color and the phosphorus and free fatty acid contents produced by the new solvent mixtures. Except for a slight increase in phosphorus, the quality of these oils is essentially similar to that of *n*-hexane or isohexane. Table 5 shows the amino acid profile (AAP) of meals produced by the test solvents, which is almost equal to that produced by *n*-hexane. The differences between these amino acid profiles seem to be limited to about 10%, when the AAP produced by the solvent mixture of isohexane/ethanol is selected as the comparison basis. The minor differences observed between the AAP values of isohexane and *n*-hexane should be confirmed by a large-scale plant test.

Abraham *et al.* (17) indicated that alcohol extraction of cottonseed, either with EtOH or IPA, may need an azeotropic distillation to regenerate the extraction solvent, owing to possible moisture transfer between cottonseed flakes and the alcohol solvent. This disadvantage of EtOH or IPA, adding azeotropic distillation to the recovery operation, is not expected in the new solvent system. It is well known that, in azeotropic distillation of water–EtOH or water–IPA system, a hydrocarbon component, such as *n*-hexane or isohexane, is used as an agent that breaks the azeotrope. Because of isohexane in the solvent mixture, a simple distillation of the three components (isohexane, water, and EtOH or IPA) is required for the recovery of the solvent mixture. A well-designed distillation column, which should easily separate water from the isohexane/alcohol mixture at any concentration, should provide regenerated alcohol, EtOH or IPA, and isohexane at the desired purity. Therefore, controlling the desired composition of the new solvent system is not expected to be a problem. Designing a distillation column for the recovery of isohexane/alcohol is a simple task, which has been practiced extensively in the oil extraction industry.

**TABLE 4**
**Physical Property of Cottonseed Crude Oils Extracted by Isohexane and Alcohol Mixtures**

| Extraction solvent (vol%) | Crude oil[a] color | Phosphorus[b] (ppm) | Free fatty[c] acid (%) |
|---|---|---|---|
| 100% Isohexane | 3.2R/40Y | 910 | 3.0 |
| 10/90% EtOH/iso-C6 | 9.4R/75Y | 1150 | 2.7 |
| 25/75% EtOH/iso-C6 | 10.2R/75Y | 1210 | 3.3 |
| 10/90% IPA/iso-C6 | 11.0R/75Y | 1140 | 2.6 |
| 25/75% IPA/iso-C6 | 12.0R/75Y | 1220 | 3.5 |
| 100% *n*-Hexane | 7.8R/75Y | 920 | 3.0 |

[a] AOCS tintometer color scale, measured with 2.5-mm path cube.
[b] By ICP (induction coupled plasma) after micro-Kjeldahl digestion.
[c] AOCS Official Method Ca 5a-40 (Ref. 15). See Tables 2 and 3 for abbreviations.

**TABLE 5**
**Comparison of Amino Acid Profile[a] of Cottonseed Meal Extracted by Hexane and Alcohol Mixtures**

| Amino acid | *n*-Hexane | Isohexane | Isohexane and 10% EtOH | Isohexane and 10% IPA |
|---|---|---|---|---|
| Arginine | 81.9 | 71.4 | 76.6 | 82.1 |
| Histidine | 19.5 | 16.6 | 17.8 | 19.7 |
| Lysine | 30.5 | 25.8 | 28.9 | 30.3 |
| Tyrosine | 20.4 | 16.3 | 19.0 | 20.5 |
| Phenylalanine | 40.1 | 33.9 | 36.6 | 40.5 |
| Methionine | 10.3 | 8.5 | 10.3 | 10.7 |
| Threonine | 22.9 | 20.4 | 21.8 | 23.2 |
| Serine | 30.3 | 26.4 | 28.6 | 31.0 |
| Leucine | 42.0 | 36.0 | 39.0 | 42.6 |
| Isoleucine | 25.2 | 18.8 | 20.3 | 22.6 |
| Valine | 31.9 | 26.0 | 28.2 | 31.5 |
| Glutamic | 135.6 | 115.4 | 126.5 | 139.9 |

[a] Grams of amino acid per 100 g of protein nitrogen.

To produce cottonseed meal and miscella-refined oil with prime bleachable summer yellow (PBSY) color, cottonseed processing may be divided into four major steps (2,8,17): (i) seed preparation (flaking, cooking and expander treatment); (ii) extraction; (iii) miscella treatment for crude oil (evaporation or distillation for solvent regeneration and miscella refining); and (iv) meal treatment (desolventizing and toasting). Because the $\Delta H$ for the new solvent system is similar to that of *n*-hexane, no retrofit is expected in the meal treatment step. The seed preparation step should be independent of the choice of extraction solvent. In the extraction step, the two key process variables to be considered are solvent amount and extraction temperature. The ratio of solvent to collet required for oil extraction with *n*-hexane is about 1, and the extraction temperature is near the boiling point of commercial hexane. Because the solubility characteristics of the newly proposed solvent system are practically identical to *n*-hexane, except for extracting gossypol, the required solvent amount is expected to be the same. The extraction temperature should also be unchanged because of the similar b.p. range (Table 3). Examining these major operation steps, one may realize that no major modification in processing conditions and equipment is required to replace *n*-hexane with the newly proposed solvent system.

As recently reported (2), isohexane has an economic advantage over *n*-hexane in cottonseed extraction. When only gossypol extraction is considered, isohexane has no advantage over *n*-hexane. Because of this intrinsic incapability of isohexane in gossypol extraction, adding 5 to 10% EtOH or IPA to commercial isohexane may provide an attractive solution to processing of cottonseed and should produce a cottonseed meal of higher quality.

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