A New Method of Detoxification of Cottonseed by Means of Mixed Solvent Extraction

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ABSTRACT

For several decades, scientists in the field of vegetable oils tried unsuccessfully to detoxify cottonseed by a practical method. By using 20-30% (by wt) of ethyl alcohol (90% in vol) with commercial hexane as a mixed solvent, we were able to extract effectively both gossypol and oil from cottonseed prepressed cake or flakes. Free gossypol in meal was reduced to ca. 0.013-0.04%; total gossypol was reduced to 0.32-0.55%; residual oil was reduced to ca. 0.5% or less. Any aflatoxin present also can be eliminated by this process. The detoxified cottonseed meal can be used as animal feed. Cottonseed protein can be used to substitute for soy protein. The extracted oil is of better quality than that obtained by the usual hexane extraction method, and gossypol is a valuable byproduct.

INTRODUCTION

Several decades ago, vegetable oil researchers began to study ways to detoxify cottonseed for animal feed. However, no practical method could be found.

Hale and Lyman reported that swine fed a 15.5% protein diet containing 0.01% or less free gossypol showed no symptoms of gossypol toxicity (1). At a free gossypol level of 0.015%, toxicity symptoms appeared but no deaths resulted. Death occurred at 0.019% and higher levels of free gossypol. Smith also reported that dietary levels of free gossypol up to 50 ppm (0.005%) may be fed without egg yolk discoloration (2). Proctor reported that the effects associated with the presence of cyclopropenoid fatty acid in the rations of laying hens have been shown to involve fatty acid metabolism, as indicated by altered fatty acid patterns of yolk lipids, pinkish discoloration of stored egg whites, pH change of stored egg yolks and whites, decreased egg hatchability and delay in the sexual maturity of hens (3). The eggs obtained from hens fed a diet with 5 ppm cyclopropenoid fatty acid showed marked improvement in quality compared to eggs obtained when the hens were fed a diet with a higher concentration of cyclopropenoid fatty acid. Hollen et al. fed calves on diets containing 28-29% protein supplied by mixtures of cottonseed meal, soybean meal and rolled oats blended to give 4 diets with free gossypol levels of 0.107, 0.071, 0.035 and 0.023%, respectively (4). The 4 calves that consumed the 0.107% free gossypol diet, and 2 of those receiving the 0.071% and the 0.035% free gossypol diets died between 49 and 120 days. Chang et al. studied chick feeding tests (5). She suggested that meals containing only small amounts of both total and free gossypol probably would be meals of exceptionally high nutritional value, provided that the solubility of the protein remained high. Vaccarino et al. used 96% acetone as a solvent to extract prepressed cottonseed cake with a residual oil content of 18-20% (6). Acetone extraction produced an exceedingly light-colored meal containing less than 0.03% free gossypol and less than 0.5% total gossypol. The oil content of the acetone-treated meal was 0.4-0.7%. Vix et al. used the liquid cyclone process to produce a degossypolized cottonseed flour with free gossypol 0.02%, total gossypol content 0.065% (7). However, the liquid cyclone process has not yet been developed successfully on an industrial scale. Ayers and Scott reported that use of commercial hexane containing 5% ethyl alcohol to extract oilseeds reduces the residual oil in the meal (8). We found the same result in our research. Rayner and Dollear reported that extracting cottonseed flakes with 90% ethyl alcohol decreases aflatoxin content 93-96% (9). Bailey indicated that gossypol dissolves easily in organic solvents such as ethyl alcohol, dissolves only slightly in petroleum ether with a higher boiling point (60-110 C) and will not dissolve in water or in petroleum ether with a lower boiling point (30-60 C) (10).

We decided to detoxify cottonseed using ethyl alcohol with commercial hexane as a mixed solvent for extraction.

EXPERIMENTAL PROCEDURES

Reagent and Raw Materials

We used 90% ethyl alcohol (vol %), commercial hexane, and expeller-pressed cottonseed cake or prepressed cottonseed cake.

Apparatus

The first extraction was done in a glass laboratory extractor (Fig. 1) whereas miscella recycling used a small batch extraction process (Fig. 2).

PROCEDURE

We broke the cottonseed cake, either pressed or prepressed, into small pieces, weighed out 100 g and placed them into the glass extractor. The water (50 C) was pumped into the jacket of the glass extractor. We then poured half of the weighed, mixed solvent into the upper preheater to be heated immediately. The cock at the bottom of the extractor was kept closed at this point, while the cock at the bottom of the preheater was opened in order to slowly

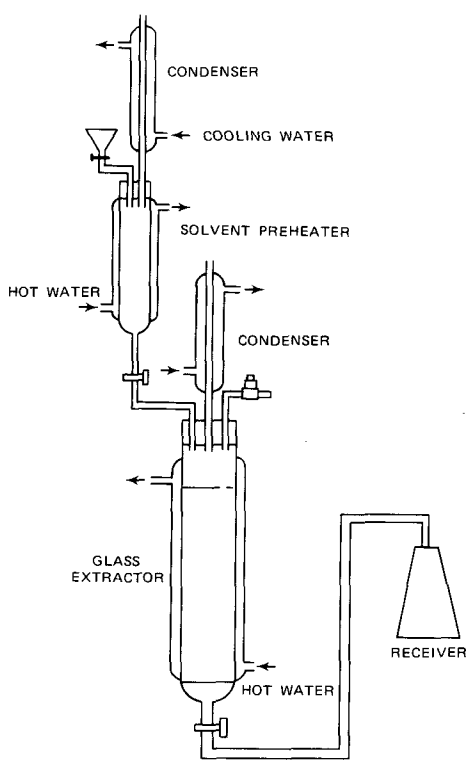

FIG. 1. Laboratory glass extraction apparatus.

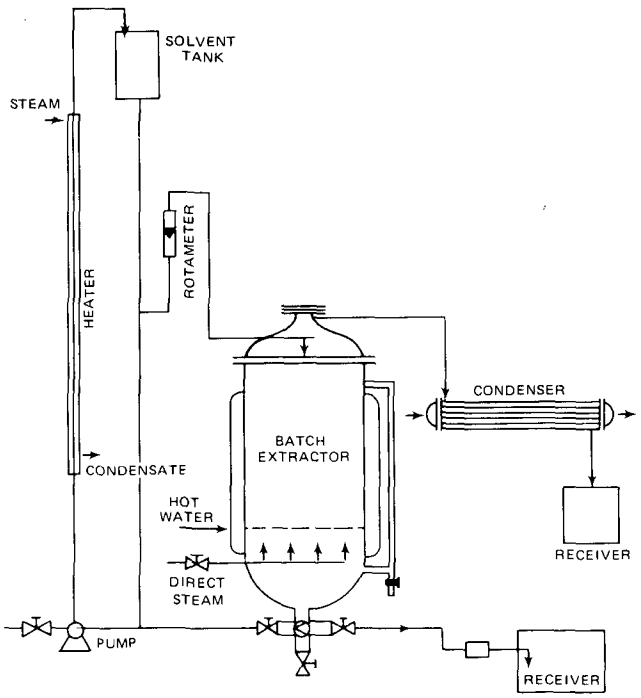

FIG. 2. Flow diagram of small batch extractor process.

pour in the mixed solvent and saturate the cake. Meanwhile, we poured the rest of the weighed, mixed solvent into the preheater and heated it. The preheated, mixed solvent soaked the cake for 30 min, then the extractor cock was opened slightly to release the extracted solution and, at the same time, the cock at the bottom of the preheater was opened to add the freshly mixed solvent so that the cake remained immersed in the mixed solvent. This process lasted ca. 60 min. The total extraction time was, therefore, 90 min. Then, all the extracted miscella and meal was released and analyzed.

Although the data in Table I are encouraging, the miscella recycle operation cannot be performed in the small glass extractor. A larger extractor must be used to achieve detoxification of cottonseed. The extraction was therefore performed in a small batch extractor (diameter 500 mm and height 1,000 mm). Figure 2 is the flow diagram of the batch extraction process. Mixed solvent was sprayed at 50 C onto the cottonseed cake until the cake was totally immersed in the solvent. The temperature of circulating water in the jacket was kept ca. 55 C. After the cake was immersed by mixed solvent in the extractor for 30 min, the valve was opened at the bottom of the small batch extractor to release concentrated miscella and at the same time, the mixed solvent was again sprayed in order to keep the cake completely immersed in the solvent. After releasing the concentrated miscella for 15 min, we changed the direction of the 3-way valve so that the miscella in the batch extractor could be pumped back and sprayed at the top of the batch extractor. This recycle operation required ca. 30 min. After the recycle operation, the spraying process was repeated for another 30 min. The total extraction time is therefore ca. 90 min. Finally, we drained the solvent contained in the meal and then used live steam to recover the solvent.

TABLE I

Percentage of Free Gossypol and Residual Oil in the Cottonseed Meal after Extraction of Expeller Prepressed Cottonseed Cake[a] by Mixed Solvent of Different Composition in a Glass Extractor

Composition of mixed solvents[b]	Free gossypol (%)		Residual oil in the meal (%)
	Wet meal	Meal after steaming	
Ethyl alcohol/commercial hexane (10:90)	0.0795	0.0555	0.47
Ethyl alcohol/commercial hexane (20:80)	0.062	0.0364	0.30
Ethyl alcohol/commercial hexane (30:70)	0.0376	0.0364	0.43
Ethyl alcohol/commercial hexane (40:60)	0.0526	0.04	0.44
Ethyl alcohol/commercial hexane (60:40)	0.0431	0.0336	2.24
Commercial hexane saturated with 90% ethyl alcohol	0.0829	0.0553	0.46

[a]Expeller-pressed cottonseed cake; free gossypol conc. = 0.09% and the residual oil in the cake = 5.9%.
[b]Concentration of ethyl alcohol = 90% vol. and the composition of mixed solvent = wt %.

DISCUSSION

A.E. Bailey indicated that gossypol is able to dissolve in ethyl alcohol. In our recent experiments, we found that by using 80% ethyl alcohol as a solvent, the cottonseed flakes thus extracted will usually contain less free gossypol than that extracted by 90% ethyl alcohol solvent. However, the defect of the 80% ethyl alcohol as a solvent is that it will reduce the extraction rate of oil by hexane, as it contains more water. We used, therefore, the 90% ethyl alcohol as a component in the mixed solvent. At room temperature, the 80-90% ethyl alcohol with commercial hexane forms 2 layers, hexane as the upper phase and ethyl alcohol the lower layer. But, at the same time, the 2 solvents tend to dissolve in each other to some extent, depending on temperature. The 90% ethyl alcohol and hexane at extraction temperature thus dissolve in each other and form one layer. After cooling, they form 2 layers again.

The data shown in Tables I, II and III prove that the mixed solvents of different composition used in extracting pressed or prepressed cottonseed cake either in a glass extractor or in the small batch extractor all achieved good results in removing gossypol. A better composition for the extraction seemed to be 20% (by wt) ethyl alcohol (90% vol) because the free gossypol in the meal thus extracted either from pressed or from prepressed cottonseed was reduced to 0.013-0.044% and the total gossypol is reduced to ca. 0.32-0.55%. The data also prove that the small batch extractor process was better than the glass extractor process. This was due to the fact that, in the batch extrac-

TABLE II

Effect of Ethyl Alcohol/Hexane Mixed Solvent in Extracting the Prepressed Cottonseed Cake in a Small Extractor

Composition of mixed solvents[a]	Prepressed cottonseed cake	
	Free gossypol (%)	Residual oil (%)
Ethyl alcohol/commercial hexane (25:75)	0.0334	0.69
Ethyl alcohol/commercial hexane (30:70)	0.035	0.39
Ethyl alcohol/commercial hexane (40:60)	0.036	0.37
Original prepressed cottonseed cake	0.149	12.2

[a]The concentration of ethyl alcohol = 90% vol.
[b]Weight of cake = 72.5 kg; the total weight of mixed solvent = 200 kg.

TABLE III

Effect of Ethyl Alcohol/Hexane Mixed Solvent Extraction of Prepressed Cottonseed Cake in a Small Extractor

Composition of mixed solvents[a]	Free gossypol (%)		Total gossypol (%)		Residual oil[d] (%)
	Wet meal[c]	Wet meal after steaming	Wet meal	Wet meal after steaming	
Ethyl alcohol/commercial hexane (20:80)	0.029	0.013	0.55	0.315	0.34
Ethyl alcohol/commercial hexane (30:70)	0.027	0.016	0.52	0.39	1.04
Ethyl alcohol/commercial hexane (40:60)	0.05	0.013	0.55	0.38	2.35
Prepressed cottonseed cake[b]	0.34	–	–	–	11.5

[a]Concentration of ethyl alcohol = 90% vol.
[b]Weight of cake in the batch extractor 40 kg; the total wt of mixed solvent = 120 kg.
[c]The wet meal after draining was used to recover the solvent with live steam.
[d]The residual oil in prepressed cottonseed cake = 11.5% and the free gossypol = 0.34%.

tor, the miscella could be recycled to create greater turbulence of the mixed solvent and thus enhance the extraction.

The quality of the cottonseed meal thus obtained entirely meets the requirements of animal feeds. In addition, the cottonseed meal, if desolventized at lower temperatures, can be substituted partially or wholly for soybean meal in making, e.g., soy sauce and foaming agents used in candy. The residual oil in the meal extracted by mixed solvent is ca. 0.5% or less. This again proves that the ethyl alcohol present in the mixed solvent is able to reduce the residual oil contained in the meal.

The fatty acid in the cottonseed oil is extracted by ethyl alcohol so that the acid number is ca. 2. Moreover, the mixed solvent can remove the gossypol and lecithin, e.g., so that the quality of cottonseed oil extracted by mixed solvent is better than that obtained by the usual hexane extraction method.

Because of the world's rapidly increasing population, scientists are worried about the protein shortage. Because cottonseed meal contains ca. 35-38% protein, the tremendous amount of cottonseed in the world, if extracted by the mixed solvent, would produce sufficient cottonseed meal for animal feeds. The resultant cottonseed protein can therefore be used as a substitute, partially or wholly, for soybean protein.

The gossypol extracted by hexane/ethyl alcohol might be used as a starting material for preparation of pure gossypol. Pure gossypol is now being used in China for birth control. The gossypol could also be used as mordant dye and in antitubercular drugs. Dianilinogossypol, a very stable compound with its antioxidant activity equal to that of gossypol on a molar basis, could be used as an antiagar in rubber industries (11). We expect, therefore, that the solvent extraction industry of cottonseed with hexane/ethyl alcohol as a mixed solvent will be further developed in the future.

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Soybean Protein Food in China

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ABSTRACT

This paper introduces the history of soybeans and soybean protein foods in China. For 4,000 years, soybeans have been one of the main crops cultivated in this country. The history of extracting protein to prepare a protein food (bean curd, tu-fu) is about 1,000 years old. Our ancestors had long been aware of the edible value of the soybean and had developed a technique for preparing many kinds of soybean foods. The traditional methods of preparing soybean protein foods such as bean curd (tu-fu), fermented bean curd (fu-ru) and dried bean milk cream (fu-tsu) are discussed.

The soybean is native to ancient China. The letters of "soybean" were found in the inscriptions on bones or tortoise shells of the Shang Dynasty (14th century B.C.). Along with wheat, rice and millet, soybeans were one of the main crops of the age. If soybean growing began at the time of the emperor Shennong, it has a history of more than 4,000 years. The cultural level was raised as economic productivity flourished. The soybean was important not only as a food but as a flavoring for food, as well. The earliest fermented soybean products were "du jiang" and "du chi." Du jiang is a fermented soy mass, and du chi is dried, fermented and salted soybeans. The preparation of these