Pre-Pilot-Plant Mixed-Solvent Flotation Process For Separating Pigment Glands From Cottonseed Meats

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Introduction

AN increased interest in the solvent extraction (5, 6, 8, 10, 11, 13) of oil from cottonseed has led to a correspondingly increased interest in methods of separation (4) and purification (1, 3) of the components of cottonseed. Attention is primarily focused on the pigments (2, 4, 9, 11) of cottonseed as an approach to the problem of obtaining an oil-free, essentially gland-free, light-colored meal.

Unlike most other oilseeds, cottonseed contains a complex pigment system (4), which, although it constitutes but 1-2% of the entire composition of the seed (11, 12), is directly responsible for the characteristic color in the final crude oil (8, 9, 11, 13) and for rendering the meal undesirable for high-grade protein feed. This pigment system occurs as a gelatinous suspension enclosed in a rigid thick walled gland (1). Microscopic examination reveals that the gland is spherical or ovoid shaped and measures 100 to 400 microns. The high mechanical strength of the gland prevents the crushing or breakage during either flaking or disintegration required to remove adhering meal tissue.

A recent publication (4) describes a laboratory method for separating flaked cottonseed into hulls, meal, and pigment glands by severe agitation followed by flotation in a liquid medium of organic solvents of definite specific gravities intermediate between the densities of the seed parts being separated. The present investigation was undertaken to develop from this laboratory method a semi-pilot plant process for the continuous removal of pigment glands from the cottonseed meats and for the purification of these two fractions for further investigation. A view towards the commercial application of the process has been maintained better to approach the problem of obtaining the quality of meal suitable for high-grade protein feed and as a source of light-colored protein for industrial utilization. The data obtained during the several experimental stages through which the investigation has so far progressed are reported herein. Engineering and technical information is presented relative to findings on fractionation of undefatted flakes as compared to defatted flakes, means of sufficiently disintegrating the flakes, the selection of suitable solvents, the effects of moisture in both solvents and flakes, the purification of pigment glands and meal, and the yields of these purified products.

A concurrent and significant development of the investigation was the production of high-purity pigment glands and of essentially gland-free meal in quantities sufficient, for the first time, to permit analytical, pharmacological, nutritional, and similar studies.

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Cottonseed and Solvents

The type, source, amounts, and analyses of the cottonseed fractionated in this investigation are shown in Table I, and the amounts and analyses of the corresponding cottonseed flakes are given in Table II.

TABLE I.

Cottonseed for Experimental Work

Type of Cottonseed	Source	Amount Processed	Moisture	Lipids as Rec'd	F. F. A. of Oil	Nitrogen as Rec'd
		lbs.	%	%	%	%
Prime Lot	E.Texas	900.0	9.75	19.12	1.20	3.27
Prime Lot No. 1	Arkansas	5403.0	11.91	17.05	1.69	2.85
Subquality Lot No. 2	Arkansas	354.0	12.29	18.37	3.83	2.88
Special Pure Bred Lot—"D & PL"	Mississippi	69.5	11.97	21.42	0.80	3.05
Special Pure Bred Lot—Delfos	Mississippi	79.0	10.99	21.18	1.00	2.92

TABLE II.

Flaked Cottonseed Meats for Experimental Work

Flakes from Following Cottonseed	Flakes Processed				
	Quantity	Defatted or Undefatted	Moisture	Lipids	Nitrogen as Rec'd
	lbs.		%	%	%
Prime Lot E. Texas	207.0	Defatted*	7.47	32.90	5.12
Prime Lot No. 1	2012.5	Undefatted	7.96	36.32	5.10
Subquality Lot No. 2	124.5	Undefatted	8.02	35.52	5.20
Special Pure Bred Lot—"D & PL"	32.3	Undefatted	7.77	37.84	4.70
Special Pure Bred Lot—Delfos	35.3	Undefatted	9.38	35.73	4.91

* The per cents moisture, lipids, and nitrogen reported are on the undefatted basis.

The cottonseed was carefully cleaned, delinted, and hulled, and the whole meats were air-purified to reduce the hull content to approximately 4% by weight. From the available meats present in the seed 60 to 65% whole meats were obtained; balance of meats was produced in the form of fines which contained a considerable amount of hulls. Whole meats, flaked to a thickness of 0.005″ to 0.008″, were used to avoid as much as possible the presence of hulls in the material for this experimental work conducted to date in the pre-pilot plant-scale equipment. The only exception was the processing of 192½ pounds of fines to determine the quality of pigment glands obtained from fines produced during preparation of the seed. It is contemplated that in full-scale pilot plant work all meats (whole and fines) will be processed.

The defatted cottonseed flakes were prepared from the prime East Texas lot by solvent extraction with Skellysolve B in a batch extractor (13), and after extraction was desolventized by air drying.

The solvents selected for the fractionation study were a commercial hexane (Skellysolve B) and perchlorethylene. These solvents have the following properties:

Commercial hexane: gravity at 60° F., 74.4° A.P.I. (Sp. gr. 0.678 at 86° F.); boiling range, 140-160° F.; Reid vapor pressure at 100° F., 5.1 pounds per square inch; evaporation residue by weight, 0.0016%; and color, water-white. Perchlorethylene: boiling point at 760 mm., 250.2° F.; specific gravity at 68° F., 1.623; refractive index, 1.5044; and evaporation residue by weight, 0.0106%. Both solvents are miscible in all proportions and were mixed in the proper quantities to obtain the desired specific gravities.

The selection of these two solvents over other solvents [such as mineral oil and carbon tetrachloride from the list of selvents found feasible for fractionation work (4)] was based on a practical and engineering point of view. Both commercial hexane and perchlorethylene have negligible effect on the rupture of pigment glands during normal fractionation operations; negligible solubility of water in either solvent, thereby minimizing the rupture of glands due to the presence of water; suitable specific gravities; and desired boiling points for fractional distillation of the two solvents. Commercial hexane is a low-cost solvent and is widely used in industry for solvent extraction of vegetable oils. Perchlorethylene is much less corrosive than, for example, carbon tetrachloride and can be safely used during normal processing in ordinary iron equipment up to 140° C. It has, besides, a low vapor pressure and its toxicity is lower than most commercially used chlorinated hydrocarbons (7).

Process Development

Numerous laboratory-scale experiments were conducted to determine the size and shape of vessels suitable for fractionation work. Using these experiments, as a basis, the process for the fractionation of cottonseed into pigment glands, meal, and hulls has progressed through four stages of development. These are described below as units (a), (b), (c), and (d). Unit (a) is illustrated in Figure 1. Figure 2 is a diagrammatic drawing of all equipment used in pre-pilot-plant development work discussed in units (b), (c), and (d). Figure 4 portrays the relative size of these three units.

Unit (a). Unit (a) consists of a glass fractionator (Figure 1) with a 5-liter blender designed to produce approximately 30 grams of pigment glands per hour from 1500 grams of defatted flakes and was operated as follows: defatted cottonseed flakes and a solvent mixture of required specific gravity of 1.378 at 30° C., compared to water at 4° C., were fed at a predetermined ratio and rate to the 5-liter glass blender equipped with a high-speed air-driven stirrer. The slurry mixture flowed continuously to the glass fractionator, the top section of which served as a means of "herding" the pigment glands. At the "herding" point the pigment glands were forced through an overflow outlet into a vacuum filter crock for removal of excess solvent. Meal and hulls settled to the bottom section of the fractionator, and subsequently into one of two meal traps from which they were discharged into suction filter crocks for removal of excess solvent. Auxiliary equipment for circulation and distillation of the filtered solvent mixture was installed adjacent to the fractionation unit. Pigment gland fractions were freed of solvent by drying in vacuum desiccators whereas the meal was dried in a pilot-plant shelf-type vacuum dryer.

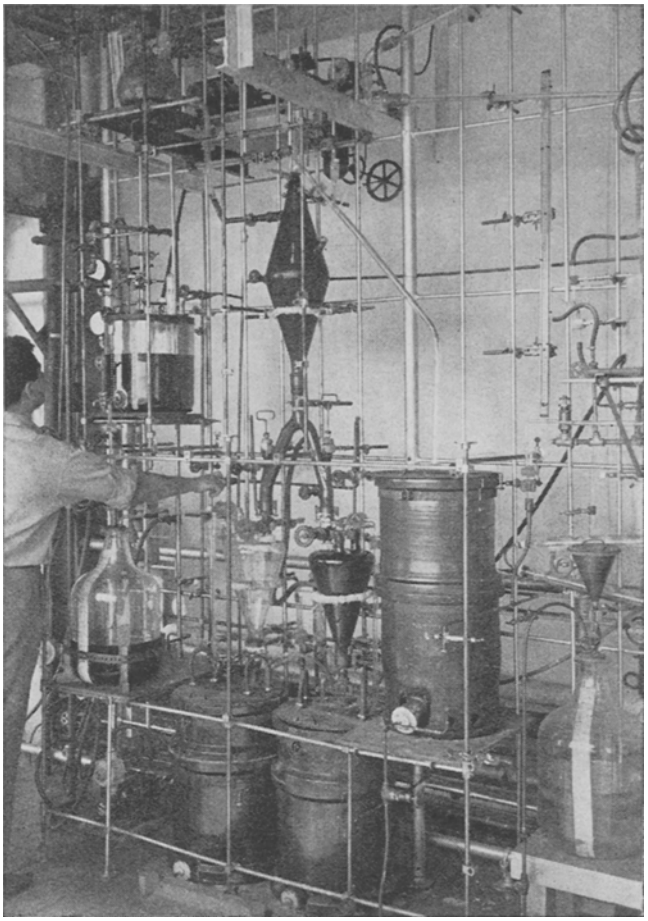

FIG. 1. Continuous glass fractionation unit.

Microscopical examinations showed that the pigment gland fraction from this operation contained

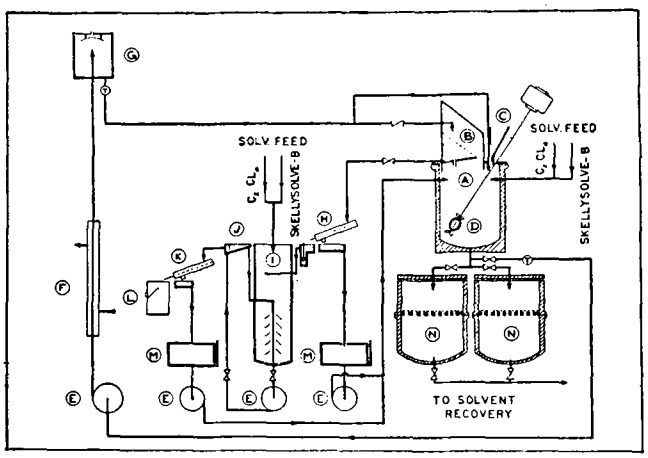

FIG. 2. Equipment for the separation of the components of cottonseed.

A	Mixing vessel (25 gal.)	I	Tank Fractionator
B	80-mesh copper screen	J	Overflow box
C	Feed hopper for C/S flakes	T	Dial thermometer
D	Blender with var. speed air motor	K	230-mesh copper screen
E	Stainless steel centrifugal pump	L	Stainless steel container (10 quart)
F	Cooler	M	Surge tank (5 gal.)
G	Stainless steel target blender	N	Vacuum filter crocks (10 gal.)
H	250-mesh copper screen		

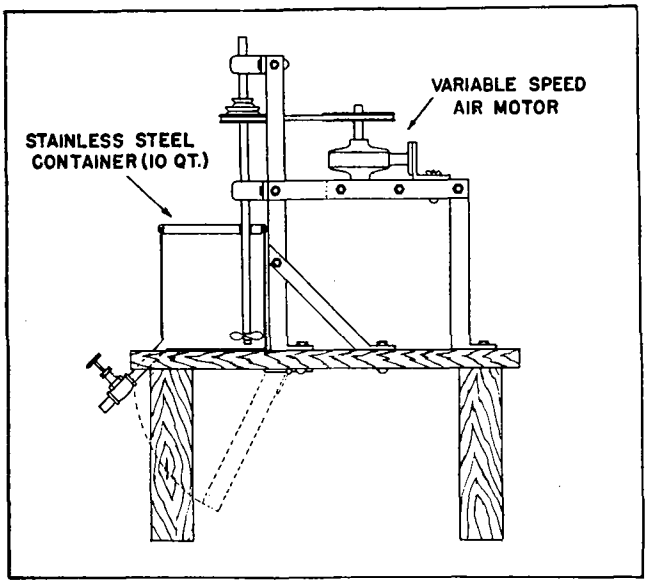

FIG. 3. Secondary blender for the purification of cottonseed pigment glands.

only 40 to 55% glands and that the gland wall was encrusted with a thin layer of what appeared to be very fine meal tissue. Since the primary interest at this stage was to obtain a pigment gland fraction of high purity for gossypol and other pigmentation investigations, purification methods and the use of undefatted flakes for fractionation were investigated.

The dried meal fraction was found to contain 25 to 40% of the original pigment glands which indicated insufficient disintegration of the flakes.

Unit (b). Unit (b) was installed and operated to obtain more efficient disintegration of cottonseed flakes; and to enable the use of undefatted flakes which, in laboratory-scale experiments, showed less incrustation of pigment glands. The first blending apparatus (A) consisted of a 25-gallon vessel equipped with an 8-inch cage type mixer (D) which was driven by a variable speed air motor (normal operating speed, 1600 to 1800 r.p.m.). The second part of unit (b), termed a "target" blender (G), functioned by discharging the mixture of meal and solvents from the 25-gallon vessel through a 1-horsepower stainless steel centrifugal pump against a 10-inch diameter stainless steel convex target fitted within a closed 10-gallon vessel. Provision was made for the rebounding slurry to flow back to the 25-gallon vessel. In order to minimize rupturing and breaking of pigment glands due to condensation of moisture within the system during blending, a precooler (F) was placed in the line for maintaining the desired slurry temperature of 20° to 26° C. This temperature was maintained at approximately 5° above the prevailing dew point temperature.

Batches of 15 pounds of defatted cottonseed meal or 18 pounds of undefatted flakes were blended with 14 gallons of solvent mixture for periods of 1 hour, with either blender, or with both blenders operating simultaneously. The simultaneous operation resulted in better disintegration. Separation of the pigment gland fraction from the meal and hulls after blending was attained by discharging the disintegrated mixture into the large suction filter crocks and allowing the mixture to settle and filter. The filtered material consisted of three distinct layers: a first, or top, layer of pigment gland fraction $\frac{1}{16}$ inch to $\frac{1}{8}$ inch thick covering approximately 60% of the area in each filter crock; second, a gummy fine-meal layer consisting of 25 to 40% of the total meal; and a third, or bottom layer containing coarse meal, with hulls located under the coarse meal but not as a distinct layer. Careful examination of the second, or fine-meal, layer showed that it was sufficiently free of pigment glands and hull particles to be acceptable as a source of meal for further purification, whereas the third (coarse-meal) layer contained some pigment glands, indicating the need of further blending of this fraction.

Unit (c). For continuous removal of the finely disintegrated meal and of pigment glands, the removable

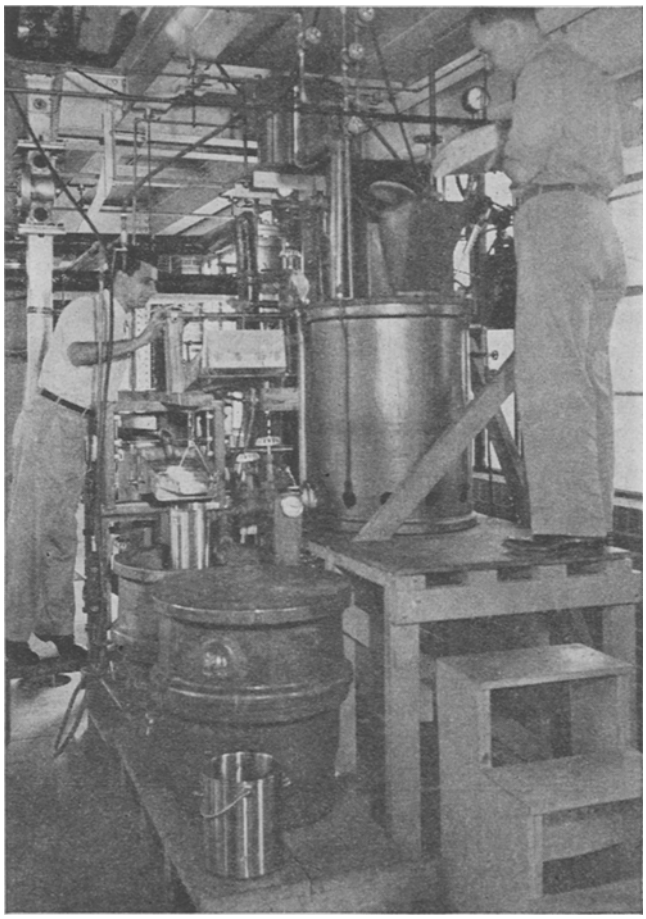

FIG. 4. Pre-pilot plant fractionation units.

80-mesh screen (B) of Unit (c) inclined at 40° angle and enclosed in a noncorrosive metal housing was placed on top of the 25-gallon blending vessel (A). The blended mixture from the target apparatus (G) flowed by gravity to the 80-mesh screen which was so constructed that the "overs," consisting of insufficiently disintegrated coarse meal and hulls, dropped back into the 25-gallon vessel whereas the "through" portion, consisting of pigment glands and finely disintegrated meal, flowed out onto a 250-mesh screen (H). The through portion from the 250-mesh screen was pumped back into the 25-gallon blending vessel. Pigment glands and fine meal collected on the 250-mesh screen were discharged into 10-quart stainless steel containers at an approximate concentration of 1 part of glands and meal to 5 parts of solvent mixture by weight. The mixture in these containers

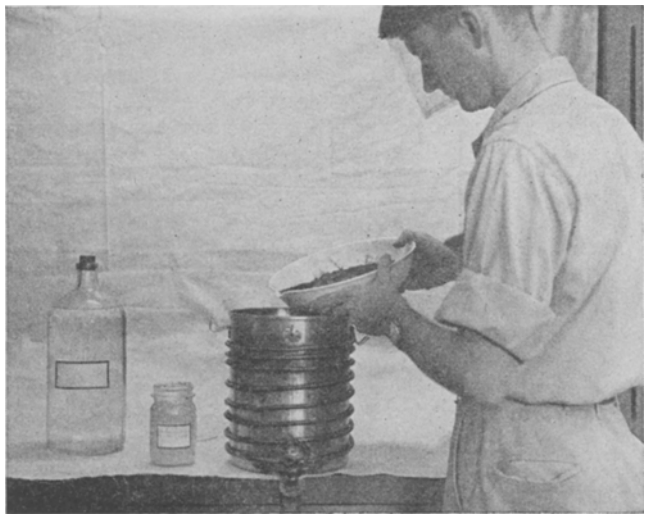

FIG. 5. Preparation for sand blending of pigment fraction.

was adjusted to a specific gravity of 1.378 and allowed to settle. The majority of the glands quickly floated to the top in a layer 1/16- to 1/8-inch thick and were collected by careful scooping and siphoning. This stage of the process was semi-continuous in that for each experiment 20 pounds of flakes together with 14 gallons of solvent mixture at the proper gravity were placed in the blending vessel and disintegration started with the two blending units previously described. Thereafter cottonseed flakes were added to the system at rates up to 2½ pounds every 5 minutes with solvent added and gravity adjusted as required during operation. Quantities of 75 to 140 pounds of flakes were processed during a normal operating day by this process.

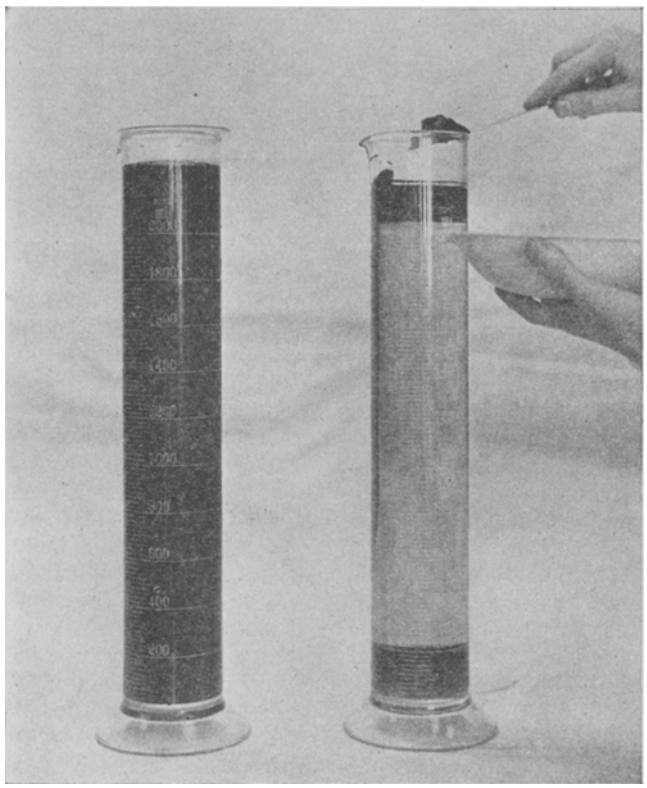

FIG. 6. Gravity separation of pigment glands and silica.

Unit (d). The 20-gallon "tank fractionator" (I) of Unit (d) was installed for the purpose of floating the pigment glands and for continuous removal of the settled fine meal fraction. This tank eliminated handling of numerous 10-quart containers as described in Unit (c). Construction of the tank (I), 12 inches in diameter and 30 inches high (Figure 2), included: baffles to minimize agitation and to facilitate the rising of glands and settling of meal; inlets at various levels to permit determination of the optimum level of entry for the pigment gland and fine meal slurry; and provisions for continuous removal of fine meal through the overflow box (J). The pigment glands and fine meal from the 250-mesh screen (H) flowed continuously into the tank fractionator at a predetermined level. The settled meal

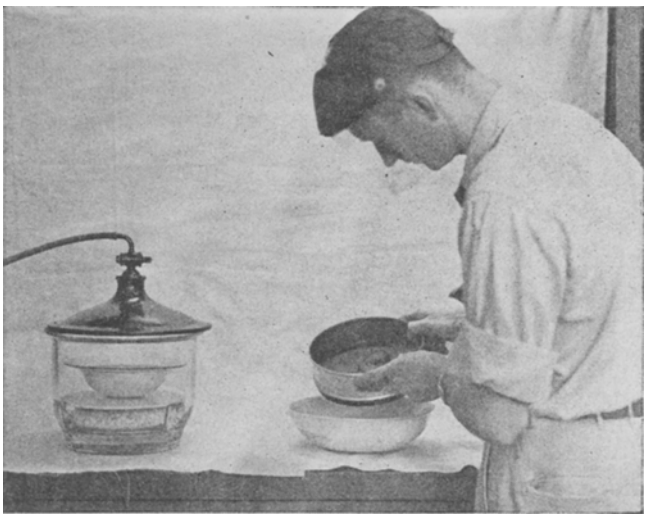

FIG. 7. Screening and drying of pigment glands.

was either pumped to or entered the overflow box by virtue of the liquid seeking its own level as the slurry was fed into the tank fractionator. The fine meal was discharged by gravity from the overflow box to a 230-mesh screen (K) where the meal was collected in 10-quart containers and the through slurry recycled back to the 25-gallon blending vessel.

Pigment glands floating to the top of the tank fractionator formed a layer 1/16- to 3/16-inch thick and were recovered by careful scooping and siphoning.

The hull and coarse meal slurry remaining in the 25-gallon blending vessel at completion of each run was drained into the suction filter crocks and allowed to settle and filter. The filtered residual material consisted of a layer of extremely fine meal (mainly the recirculated portion passing through the 250- and 230-mesh screens) and a hull and coarse-meal layer, with the hulls at the bottom of the coarse meal but not as a distinct layer. The fine and coarse meals collected in the filter crocks together constituted but a small fraction of the original flakes.

During this last stage of development several types of stirrers were investigated for blending in the 25-gallon blending vessel, e.g., propellers, basket-type mixers, impeller-type dissolvers, and a combination of the first with either of the last two. The best results were obtained with the two following combinations: a dissolver-type stirrer with a right hand and left hand propeller mounted on the shaft directly above and below the dissolver; or the two propellers

mounted with a special basket-type mixer in between the two propellers. The propellers moved the slurry toward the stirrers.

A double run was attempted, i.e., continuance of the fractionation procedure a second day without emptying the contents of the tank fractionator, in order to determine the feasibility of operating for long periods of time with the existing fractionating units. Operations during the first day were normal, but on the second day a large proportion of glands appearing with the fine meal fraction indicated the necessity of rapid separation of pigment glands and meal in commercial operations.

Purification of Meal and Pigment Glands

Meal. Purification of the fine meal fraction from experimental runs in units (b), (c), and (d) was accomplished by reblending the fine meal from each run in a 75-gallon tank with solvent mixture having a specific gravity of 1.378. The slurry was allowed to settle and the small quantity of "slow-rising" pigment glands on the surface were periodically removed by siphoning. Higher gravities (up to 1.390) were used during the later experiments to facilitate rising of pigment glands. The essentially gland-free meal was recovered by filtering the slurry through 10-gallon suction filter crocks and then drying in a tray vacuum dryer (See Figure 8). The residual oil (5-8%) remaining in the meal at this stage of the process was extracted with Skellysolve B in a batch extractor (13). Solvent-wet meal from both the filter crocks and from the extractor contained 40 to 60% solvent by weight. After redrying in the tray vacuum dryer the extracted meal was submitted for pharmacological, nutritional, and other studies.

Vacuum drying procedure for the meal was as follows: the reblended, filtered meal, containing both Skellysolve B and perchlorethylene, was spread in layers 1- to 1½-inch thick in trays of dryer. After slowly evacuating the dryer, a reduced pressure of 24 inches of mercury was maintained during the drying operation. Steam was passed through the trays until the steam pressure within the shelves was 15 pounds and the temperature of the meal was increased from 165° to approximately 220° F. Total time for the drying procedure was about 5 hours. The drying time required for meal containing only Skellysolve B (for example, meal after solvent extraction of the residual oil) was about 2 hours.

For removal of solvent from meal without subjecting it to temperatures above 125° F., two variations in the purification and drying procedures were required: first, the meal after reblending and filtering was thoroughly washed with Skellysolve B to remove the perchlorethylene (which has a boiling point of 250° F.), and second, in drying the meal hot water at a temperature of 110°-120° F. was circulated through the shelves of the tray vacuum dryer (Figure 8) instead of steam. The total time for drying this meal was approximately 4 hours.

Pigment Glands. Microscopical examinations showed that purification of pigment gland fractions by removal of adhering and encrusting meal tissue by sand blending in a mixture of Skellysolve B and perchlorethylene was obviously necessary to produce pigment glands sufficiently clean for investigational purposes.

Numerous laboratory experiments were conducted using various combinations of Skellysolve B, perchlorethylene, carbon tetrachloride, mineral oil, and cottonseed oil with glass beads, sand, silicon carbide, soap, ethyl alcohol, sodium hydroxide, sodium phosphate, and 300-mesh silica. The best results were

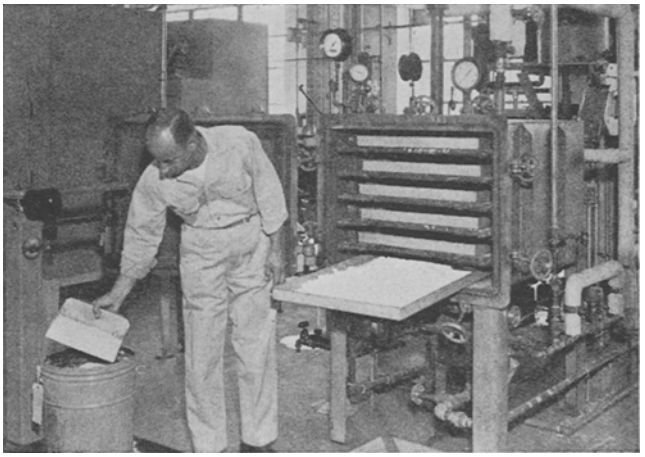

FIG. 8. Vacuum tray dryer for desolventizing cottonseed meal.

obtained by blending the glands with 300-mesh silica in Skellysolve B or in solvent mixture (sp. gr. 1.378) used for flotation. Blending with silica cuts off some of the encrusted meal tissue (1).

On the basis of the above work, the following purification procedure has yielded 1.6 to 3% pigment glands on an oil-free, moisture-free basis from undefatted cottonseed flakes and with a final purity of 80 to 85% pigment glands in the final pigment gland fraction:

1. Sand blending of pigment glands in a mixture of 200 cc. of Skellysolve B and perchlorethylene mixture with specific gravity of 1.378 and 300 grams of 300-mesh silica for 45 minutes with a 2½-inch diameter propeller driven at 2000 r.p.m. with an air driven motor (See Figures 3 and 5).
2. Gravity separating the pigment glands from the silica and detached meal (See Figure 6).
3. Wet-screening with 230-mesh copper screens and washing the purified glands two or three times with Skellysolve B for further removal of meal from detached glands (See Figure 7).
4. Drying the pigment glands under vacuum in a vacuum desiccator.

Experimental Results

Data from Units (a)-(d). The pigment gland yields obtained with the various units (a) to (d) are shown in Tables III to X. The purity of the gland fraction in the following tables was estimated on the basis of microscopic examination which revealed the approximate quantity of free meal, or adhering meal tissue on the glands, and from this examination the per cent glands by weight in the fraction was determined.

Table III shows the results of the experimental fractionation of defatted cottonseed in the glass fractionation system. The essential change in the operation of unit (a) for these experiments was the method for disintegration of the flakes prior to fractionation. The 5-liter glass blender, equipped with agitator (speed 2000 r.p.m.) in this unit, was operated for Experiments Nos. 1 and 2. For Experiment No. 3 flakes were pulverized in a Raymond high-speed swing hammer mill prior to blending in the 5-liter

TABLE III.

Data for Experiments in Unit (a) with Defatted Cottonseed Flakes from Prime Lot—East Texas

Experiment No.	Defatted Cottonseed Processed			Pigment Glands		
	Lbs.	% Moisture	% Oil	Fraction Wt. Gms.	Glands Wt. Gms.	Yield %*
1	30.0	11.0	1.3	166	84	0.704
2	17.0	11.0	1.3	109	54	0.799
3	27.0	11.0	1.3	253	152	1.415
4	9.6	10.6	0.6	127	83	2.11
5	4.2	10.6	0.6	82	33	1.93
6	10.6	10.6	0.6	229	91	2.13
Total	98.4			966	497	

* Yields are on oil-free, moisture-free basis.

glass blender. These pigment glands were completely encrusted and the procedure used was ruled as undesirable for preparing pigment glands free of adhering tissue, but might be useful for removal of glands from seed extracted with hydrocarbon solvents. For Experiments 4 to 6, Waring Blendors were operated to disintegrate the flakes, and the slurry was uniformly fed into the fractionator. The glands processed in Experiments Nos. 4 to 6 were better in quality to those obtained from Experiments Nos. 1 to 3. However, the former still contained considerable amounts of encrustation and adhering meal tissue. Experimentation with the unit (a) resulted in the adoption of the first stage of batch blending operation as described under unit (b).

TABLE IV.

Data for Experiments in Unit (b) with Defatted Cottonseed Flakes from Prime Lot—East Texas.

Experiment No.	Defatted Cottonseed Processed		Pigment Glands		
	Lbs.	% Moisture	Fraction Wt. Gms.	Glands Wt. Gms.	Yield %*
1	15	10.57	89.3	53.6	0.88
2	15	10.57	119.3	71.6	1.19
3	15	10.57	124.0	74.4	1.23
4	15	10.57	111.3	75.2	1.25
5	10	10.57	59.3	35.6	0.88
Total	70		503.2	310.4	

* Yields are on oil-free, moisture-free basis.

TABLE V.

Data for Experiments in Unit (b) with Undefatted Cottonseed Flakes from Prime Lot No. 1—Arkansas.

Experiment No.	Undefatted Cottonseed Processed		Pigment Glands		
	Lbs.	% Moisture	Fraction Wt. Gms.	Glands Wt. Gms.	Yield %*
1	18	8.19	132.5	72.2	1.59
2	18	8.19	107.3	73.2	1.62
4	18	8.19	110.0	87.3	1.93
5	18	8.00	110.6	90.3	1.99
6	18	4.80	111.6	89.3	1.90
Total	90		572.0	412.3	

* Yields are on oil-free, moisture-free basis.

Table IV gives the results of the first experiments conducted in unit (b). Only the blender in the 25-gallon vessel was operated. No increase in yields of glands was obtained over experiments given in Table III, but larger quantities of material could be processed during the same period. In addition, better purification of the glands was accomplished by the adoption of the method of wet screening the gland fractions through 100- and 230-copper mesh screens to remove, respectively the large and small meal particles. The glands obtained had a relatively undesirable amount of adhering or encrusting meal tissue, however, the screening procedure aided in producing a better product.

Table V shows the results for the first group of experiments using undefatted cottonseed flakes. Considerably better yields were obtained than for the experiments listed in Table IV. The principal difference in processing was the operation of the target blender in conjunction with the 25-gallon batch blender. In addition, an improved purification process was adopted consisting of sand blending with 300-mesh silica with screened pigment glands (through 100-mesh) in a continuous shaker. The effect of this improvement is illustrated in the increased average purity of the glands as given in Table V as compared with those given in Tables III and IV. Excessive high humidity conditions prevailed during Experiment No. 3 (results not included in Table V). A pigment gland yield of only 0.94% was obtained for this experiment. Moisture condensed into the system and caused rupturing of pigment glands.

TABLE VI.

Data for Experiments in Unit (b) with Predried Undefatted Cottonseed Flakes from Prime Lot No. 1—Arkansas.

Experiment No.	Undefatted Cottonseed Flakes			Pigment Glands		
	Lbs.	% Moisture		Fraction Wt. Gms.	Glands Wt. Gms.	Yield %*
		Before Drying	After Drying			
1	15.0	8.2	5.3	103.6	80.2	2.06
2	18.0	7.6	4.9	117.9	92.1	1.97
3	18.0	8.2	5.7	118.5	94.0	2.02
4	19.5	8.8	5.8	138.2	107.0	2.13
5	18.5	7.3	4.5	105.3	83.1	1.76
6	19.5	7.9	5.3	125.2	99.4	1.96
7	19.5	8.2	4.7	140.4	110.9	2.17
8	19.5	8.2	6.1	118.4	88.5	1.76
9	22.0	8.1	5.5	166.2	123.1	2.16
10	24.0	8.4	5.8	192.1	134.6	2.17
11	26.0	8.6	5.4	161.0	118.4	1.82
Total	219.5			1486.8	1131.3	

* Yields are on oil-free, moisture-free basis.

The results reported in Table VI show slightly higher and more consistent yields than those obtained from the previous series of experiments. These experiments were conducted in the same manner as used for experiments listed in Table V, with the following exceptions: The flakes prior to fractionation were dried in a tray dryer with parallel flow of hot air (125° F.) across the trays to reduce the moisture content of flakes to the amount shown in the table. This drying operation apparently facilitated disintegration of the flakes and minimized the accumulation and effect of moisture or free water in the system.

Table VII shows the results obtained with the improvements in the fractionation system as described for unit (c). Gland fractions obtained were purified by sand blending in secondary blender (Figure 3) and by further screening and washing. Considerably larger quantities of material were processed and higher yields and purity of glands were obtained than in the previous experiments.

The equipment operated and processes employed to obtain the results reported in Table VIII were the same as for the experiments listed in Table VII. Experiments Nos. 1 and 2 show the effect of not drying the flakes processed from Prime Seed Lot No. 1—Arkansas prior to fractionation. In Experiments Nos. 3 and 4, the flakes were prepared from fines produced in the preparation of whole meats from Prime Seed (Lot No. 1—Arkansas). The quality and quantity of the glands obtained for these two experiments were

TABLE VII.

Data for Experiments in Unit (c) with Predried Cottonseed Flakes (125° F.) from Prime Lot No. 1—Arkansas.

Experiment No.	Undefatted Cottonseed Flakes			Pigment Glands		
	Lbs.	% Moisture		Fraction Wt. Gms.	Glands Wt. Gms.	Yield %*
		Before Drying	After Drying			
1	28.0	7.7	5.6	206.3	157.1	2.17
2	36.0	5.3	3.7	277.9	209.9	2.20
3	54.0	8.1	4.6	394.3	303.5	2.15
4	54.0	7.7	4.9	542.9	398.5	2.83
5	72.0	7.2	2.8	744.4	583.7	3.04
6	66.0	7.6	4.0	623.2	496.8	2.86
7	71.5	8.6	3.6	693.3	554.6	2.93
8	86.0	8.6	5.2	828.3	652.8	2.93
9	130.5	8.8	5.4	1173.1	930.0	2.76
Total	598.0			5483.7	4286.9	

* Yields are on oil-free, moisture-free basis.

comparable to those in Table VII; however, the meal portions contained a considerable amount of fine hull particles. No further experiments were conducted with this type of material.

TABLE VIII.

Data for Experiments in Unit (c) with Cottonseed Flakes from Various Lots.

Experiment No.	Undefatted Cottonseed Flakes			Pigment Glands		
	Lbs.	% Moisture		Fraction Wt. Gms.	Glands Wt. Gms.	Yield %*
		Before Drying	After Drying			
1	28.0	7.6	Not dried	185.9	139.6	1.96
2	76.0	7.3	Not dried	415.2	307.3	1.94
3	84.0	8.9	5.4	780.0	601.0	2.76
4	108.5	9.4	5.0	860.1	684.2	2.42
5	32.3	7.6	5.2	223.5	178.7	2.18
6	35.3	9.5	5.5	223.9	179.1	1.97
7	124.5	8.2	4.3	1110.8	873.3	2.69
Total	488.6			3799.4	2963.2	

* Yields are on oil-free, moisture-free basis.

For Experiments Nos. 5 and 6 the flakes were prepared from the special pure bred lots, "D & PL" and "Delfos." Microscopic examination revealed that the glands from these materials were essentially the same quality as those from the prime cottonseed. These pure bred lots were processed for special laboratory investigation of the pigment glands produced. The experimental yields of pigment glands from these special lots were 2.18 and 1.97% as shown in Table VIII above. The theoretical yields of pigment glands were 2.92 and 2.18%, respectively, and were calculated on the basis of the ratio of gossypol content of flakes and of separated pigment glands. The theoretical content of glands in the commercial seeds was not calculated because of the heterogeneity of original flakes.

Experiment No. 7 gives the results obtained with undefatted flakes from whole meats prepared from a subquality lot of cottonseed (See Tables I, line 3, and II, line 3). Although the pigment glands processed were comparable to those obtained from prime lots of seed, difficulty was experienced in getting the desired flotation of glands from the subquality lot, with the result that gland-free meal from this lot was not easily obtainable.

An attempt was made to process in unit (c) defatted cottonseed flakes, immediately after extraction of oil without removal of absorbed Skellysolve B. Blending difficulties were encountered due to the different characteristics of this material as compared to those of undefatted flakes. The glands obtained were purified by the same procedure as used for experiments given in Table VII; however, the purified glands had considerably more adhering meal tissue than those from undefatted cottonseed flakes. In view of these results it is believed that this type of material is less suitable for fractionation work or preparation of pure pigment glands.

Table IX gives the results of the process used in conjunction with operation of unit (d) as illustrated in Figure 2. The purification procedure for gland fractions was identically the same as used for experiments in Tables VII and VIII. The operation of this equipment [unit (d)] demonstrated that improvements other than the tank fractionator are required for efficient and rapid separation of the pigment glands by this liquid flotation principle. The operation of this system furnished engineering information relative to the behavior of the glands and meal during large-scale fractionation operations. Yields obtained are somewhat lower than those given in Table VII.

Pigment Glands Produced. Eighty-three per cent of 41.6 pounds of total gland fraction given in Table X had a purity of 80 to 85% and was suitable for pharmacological, nutritional, analytical, and other investigations.

Careful microscopic examination of glands showed approximate amounts of free, adhering, or encrusted meal and revealed the true color of the glands. It was observed that the glands from defatted cottonseed meal were a deep red and purple color. The pigment glands from undefatted cottonseed (Prime lot No. 1—Arkansas) varied in color from a light orange and red to a dark red and deep purple over a period of four months.

Analyses of the purified gland fractions showed a gossypol content of 36 to 41%; moisture, 5.8%; oil as received, 5.4%; nitrogen, 1.89%; and silica, 0.55% (from sand blending purification procedure).

Table X reports the average per cent purity and per cent yield of glands for the total material processed as given in each of Tables III through IX, with exception of Table VIII. (Since Table VIII shows results for various lots of cottonseed, no attempt was made to average the results.)

TABLE IX.

Data for Experiments in Unit (d) with Predried Cottonseed Flakes from Prime Lot No. 1—Arkansas.

Experiment No.	Undefatted Cottonseed Flakes			Pigment Glands		
	Lbs.	% Moisture		Fraction Wt. Gms.	Glands Wt. Gms.	Yield %*
		Before Drying	After Drying			
1	67.5	8.8	4.3	437.2	339.1	1.82
2	120.0	8.6	4.9	930.6	707.2	2.26
3	117.0	8.6	4.6	912.2	663.0	2.17
4	140.0	8.5	5.3	900.4	678.3	1.89
5	120.0	7.4	5.9	954.7	735.4	2.38
6	226.0	7.4	5.7	1936.1	1440.0	2.46
Total	790.5			6071.2	4563.0	

* Yields are on oil-free, moisture-free basis.

Meal and Oil Produced. In the earlier experiments of this investigation emphasis was placed on pigment gland production, but as the fractionation process was developed the processing of a meal fraction was worked out.

A total of 564 pounds of powdery, light-yellow-colored meal (3), practically free of hulls, oil, and pigment glands, was actually produced from 1712 pounds of undefatted cottonseed flakes. The calcu-

lated yield of hull-free, essentially pigment-free, and oil-free meal from 1712 pounds of flakes is 884 pounds of meal. The calculation is based on an oil content of 37.7%, moisture content of 4.7%, pigment gland content of 2.0%, and hull content of 4.0%. This shows a recovery of 63.8% of the available meal. The losses are due mainly to the many transfers made in processing and to some coarse meal not sufficiently disintegrated during the blending operations, both of which can be improved with further experimentation.

The purified meal which was practically free of pigments, oil, and hulls had a gossypol content (spectrophotometrically determined) as low as 0.006%; oil on "as is" basis of 0.5%; moisture, 6.0%; and nitrogen, 9.0%.

For special investigational work, approximately 100 pounds of the 564 pounds of meal were desolventized at 120° F. to avoid high temperatures which may have deleterious effect on use of the meal in nutritional and other investigations.

TABLE X.

Cottonseed Flakes Processed and Per Cent Yields.

Table No.	Lbs. Processed	Pigment Glands			
		Fraction Wt. Gms.	Glands Wt. Gms.	Purity % (Average)	Yield %** (Average)
III	98.4	966.0	497.0	51.4	1.25
IV	70.0	503.2	310.4	61.8	1.11
V	90.0	572.0	412.3	72.1	1.81
VI	219.5	1486.8	1131.3	76.2	1.99
VII	598.0	5483.7	4286.9	78.2	2.73
VIII	488.6	3799.4	2963.2	X	X
IX	790.5	6071.2	4563.0	75.0	2.2
Total	2355.0	18,882.3*	14,164.1		

* Equivalent to 41.6 pounds.
** Yields are on oil-free, moisture-free basis.

Crude cottonseed oil miscella from the mixed-solvent flotation process developed was steam stripped and vacuum dried (13) to remove solvent and moisture. The resulting oil was successfully refined by modified official American Oil Chemists' Society methods for hydraulic-pressed oils (13), and bleached by the official A.O.C.S. methods (6% fuller's earth). The colors of the refined oils varied from 35Y-5.0R to 35Y-6.1R and for the bleached oils from 15Y-1.5R to 20Y-1.0R. All are prime colors. The refining losses varied from 6.8 to 8.4%.

Although the crude cottonseed oil from the mixed-solvent flotation process had a characteristic odor, a deodorized sample of this oil was found to be bland, practically odorless, and comparable to deodorized oils of good quality produced from hydraulic-pressed cottonseed oil. The stability of this oil, determined by the Active Oxygen Method at a temperature of 97.7° C., showed a keeping time of 12.5 hours (time required for the peroxide value of the oil to reach 100 milliequivalents per kilogram). This stability is comparable to other good cottonseed oils and, according to data in the literature, an oil having a keeping time of 12.5 hours at 97.7° C. in the accelerated test might be expected to have a shelf life of two to four months when stored at 70° F.

Serious consideration is warranted for the installation of a full-scale pilot plant to determine whether this liquid flotation process can be used at a reasonable cost to obtain both a cottonseed oil comparable in grade to that produced by other methods and a light-colored meal suitable as a high-grade protein feed and as a source of light-colored protein for industrial utilization. Pigment glands will be a by-product of the process.

Conclusions

1. Undefatted cottonseed flakes are preferred over defatted cottonseed flakes for fractionation work for the following reasons:
   a. Better yields and quality of glands are obtained.
   b. The glands are more readily freed of the tenaciously adhering meal tissue.
   c. The overall time of contact during processing of pigment glands with solvent is shortened, thereby minimizing the rupturing or breaking of some of the glands.
   d. Solvent extraction of the oil can be concurrently carried out while separating the pigment glands from the meal.
2. Undefatted flakes from prime lots of cottonseed are more easily separated into their components than are those from a subquality lot.
3. Upon storage the pigment glands undergo some change. The pigment glands processed and purified from a prime lot of cottonseed were of light orange and red color during the early phase of this investigation. The color of glands similarly obtained four months later was dark red and purple.
4. Moisture and temperature during operation are important for minimizing the rupturing of glands and for more efficient disintegration of flakes, particularly when highly humid conditions prevail.
5. The development of the process reported was on a sufficient scale to produce large enough quantities of purified pigment glands and light-colored, powdery meal (practically free of hulls, oil, and pigments) for pharmacological, nutritional, analytical, and other investigations.
6. Sixty to 70% of the oil content of the flakes can be recovered as a miscella (approximately 10% oil by weight) while separating the glands from the meal. The remaining amount of oil can be extracted by countercurrently passing the solvent mixture through the partially defatted cottonseed. The effluent (low oil content miscella) could be adjusted to the proper gravity and then used directly in the process for removal of pigment glands.
7. The shelf-type vacuum dryer was suitable for removing the solvent from the meal for pre-pilot plant experiments. A suitable process for removing the solvent from the meal on a large scale remains to be developed.
8. The large-scale production of prime oils and light-colored meal from prime lots of cottonseed is possible if the following operations are quickly and successively conducted: a quick disintegration of the cottonseed in the solvent mixture; a rapid, efficient removal of the pigment glands from the meal; and the production of a miscella from which the oil can be recovered by normal oil and solvent recovery processing.
9. Cottonseed oil prepared by the mixed-solvent flotation process was successfully refined by slightly modified American Oil Chemists' Society (A.O.C.S.) refining methods which yielded oils of prime color.

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The Amplified Distillation of Methyl Esters of Fatty Acids*

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Introduction

ACCORDING to the theory of distillation the components of a volatile mixture may be separated from each other in any desired approach to purity. It is only necessary to provide sufficient theoretical plates.

In the application of fractional distillation to analytical work certain practical limitations must be considered. If a large number of theoretical plates is required for a given separation, it follows that a correspondingly large amount of a given component must be present before any is available for separation at the desired purity. The reason for this is that as a cut point is approached and passed, there is a gradual change in the composition of the distillate from lower boiling component to higher boiling component. The amount of this inseparable mixture is a function of the column hold-up per theoretical plate.

Amplified distillation is a technique by which the interjacent mixtures inevitably encountered in ordinary fractional distillation may be eliminated in certain specific instances. This permits a more nearly complete separation of the components in the desired purity and is especially useful in case certain components occur in small proportions or in case the sample is of limited availability. Amplified distillation does not alter the efficiency of a given still but merely allows the full efficiency of the still to be developed with respect to the separation of each component, regardless of the amount or proportion present in a given mixture.

In amplified distillation an additional component is introduced. This component is so selected that it distills between the components of the mixture and is easily distinguishable and separable from them. For the amplified distillation of methyl esters a hydrocarbon mixture of petroleum origin meets these requirements and has the added advantages of a smooth true boiling point curve and ready availability. It is only necessary to select a commercial product having the appropriate distillation range.

Amplified distillation should not be confused with azeotropic distillation in which the desired effect of the added component is to alter the partial vapor pressures of the components of the mixture differently. Azeotropic distillation is usually employed for the separation of dissimilar substances having similar boiling points. Amplified distillation is useful in the separation of similar substances such as adjacent members of homologous series or structural isomers.

The idea of amplified distillation is not new. Bratton, Felsing, and Barley (1) used kerosene to enhance the separation of certain petroleum bases. In this case, in addition to the advantage of dilution, the spread between the boiling points of the bases was increased fortuitously due to azeotrope formation. Later Axe and Bratton (2) extended the method to the separation of binary mixtures of homologous fatty acids such as propionic and butyric. They reported a maximum recovery of pure acid in only 73% yield, due to limited efficiency of their distillation equipment. In this case the formation of azeotropes with the hydrocarbon diluent probably hindered the separation.

Apparatus and Materials

The laboratory vacuum distillation apparatus used in this investigation was identical with that described in an earlier paper (3) except for the substitution of a more efficient, spiral-conical-pattern, wire gauze packing (4). The packed section was 44 inches in length by one inch inside diameter. The overall efficiency was approximately 100 theoretical plates. Distillations were carried out at a head pressure of 2 mm.

Two commercially available mineral oils were used as diluents: Eureka White Oil (55 Seconds Saybolt Universal Viscosity at 100° F.) and Mineral Seal Oil (42 Seconds Saybolt Universal Viscosity at 100° F.).

Amplified distillations were carried out on palmitic acid, "double distilled cottonseed fatty acid" and the methyl esters of the cottonseed fatty acids. Palmitic acid was obtained by hydrolysis of a heart cut of methyl palmitate and was recrystallized to a constant melting point of 62.6° C. The "double distilled cottonseed fatty acid" was a commercial material. The methyl esters were prepared by refluxing the acid with anhydrous methanol saturated with hydrogen

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