Isopropanol as a Solvent for Extraction of Cottonseed Oil.[1] II. Separation of Purified Oil From Miscella

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IN developing a process for solvent extraction of edible oil-bearing seeds the prime objects are to produce a superior quality meal and a premium grade oil by economical methods. In the first paper on this subject (1) the possibility of accomplishing these objects by the use of isopropanol as a solvent in the extraction of cottonseed oil was discussed. Isopropanol was shown to extract efficiently both oil and gossypol and to produce a meal having considerably greater nutritional value for swine and rats than hydraulic meal (2). The protein in the meal is not denatured in the process and therefore may be used for industrial purposes. Another advantage in the use of isopropanol for the extraction of cottonseed oil lies in its property of coagulating the fine meal particles which tend to cause trouble during extraction of the oil and drying of the meal.

When cottonseed meats are extracted with hot 91-95 volume per cent isopropanol, the miscella contains, in addition to the oil, considerable gossypol, resins, color bodies, carbohydrates, phospholipids, fatty acids, and lesser amounts of sterols and tocopherols. The quantity of non-oil extractives, exclusive of fatty acids, varies between 10 and 16% of the total extract. Lower concentrations of isopropanol extract more carbohydrates, thus increasing the non-oil extract. If the solvent is stripped from this miscella, some of the impurities will separate as foots but a large amount will remain dissolved in the oil. The oil will therefore be dark, difficult to refine, and have a high refining loss.

When the miscella is cooled to room temperature, relatively pure oil separates. This oil is readily refined with a low loss. The fatty acids and other impurities remain predominantly in the isopropanol-water phase along with a significant quantity of oil. If liquid-liquid extraction principles are applied to this phase separation, it is possible to separate the oil almost completely from the non-oil extractives.

The purpose of these investigations was to develop a method for efficient separation of a high quality oil from the isopropanol extract of cottonseed.

Solubility Data and Equilibrium Data

The System: Isopropanol-Water-Cottonseed Oil-Oleic Acid. At the start of these investigations it was considered that the fatty acids would have solute properties more similar to pure cottonseed oil than the other impurities dissolved in the oil. Accordingly oleic acid was chosen as the key component to be separated from the oil in developing a liquid-liquid extraction procedure for purification of the oil. Comparative solubility tests with linoleic acid have shown that its solute properties are almost identical with those of oleic acid, and it is believed that the latter acid can well represent the free fatty acids normally occurring in cottonseed.

Solubility data for mixtures of oleic acid and caustic refined oil in isopropanol were obtained by the cloud point method. In this method the solute is stirred into the solvent at constant temperature until the formation of a slight cloudiness indicates phase separation. All of the solubility data were determined at 30°C.

Data for the solubility of various mixtures of oleic acid and cottonseed oil in aqueous isopropanol are presented in Fig. 1. The compositions of the oil and

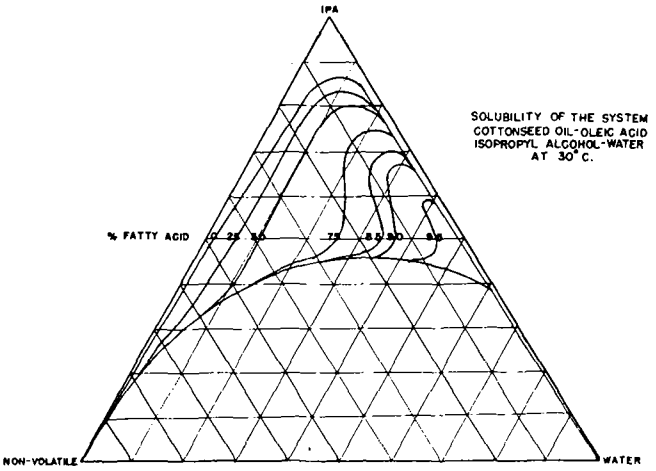

FIG. 1

acid on a solvent free basis are plotted as parameters and the spaces below the curves represent the insoluble region. It may be noted that in order to obtain a phase separation of mixtures containing high acid concentrations, lower alcohol concentrations are necessary. For example, with an oleic acid of 85% the alcohol concentration should be less than 70% to insure the formation of two phases.

Equilibrium distribution of the oil and oleic acid between phases was obtained by making up a mixture of the components known to be in the insoluble range and permitting separation to take place at 30°C. The relative quantity, the per cent non-volatile, the per cent oleic acid, and the specific gravity were determined for each phase.

The effect of isopropanol concentration on the distribution of oleic acid between phases is shown in Fig. 2, Curves 1, 2, 3. For each of these curves the isopropanol-water ratio in the system was maintained constant. It is apparent that the degree of separation of fatty acid from oil is very favorable and is greater with the low alcohol concentrations. For extraction of the acid however the lowest practical concentration is between 60% and 70% since the density of the alcohol phase approaches that of the oil phase at 50% isopropanol. Phase mixtures having alcohol concentrations below 60% formed dispersions which were very difficult to separate.

From the foregoing discussion, it is apparent that the optimum concentration of isopropanol for separa-

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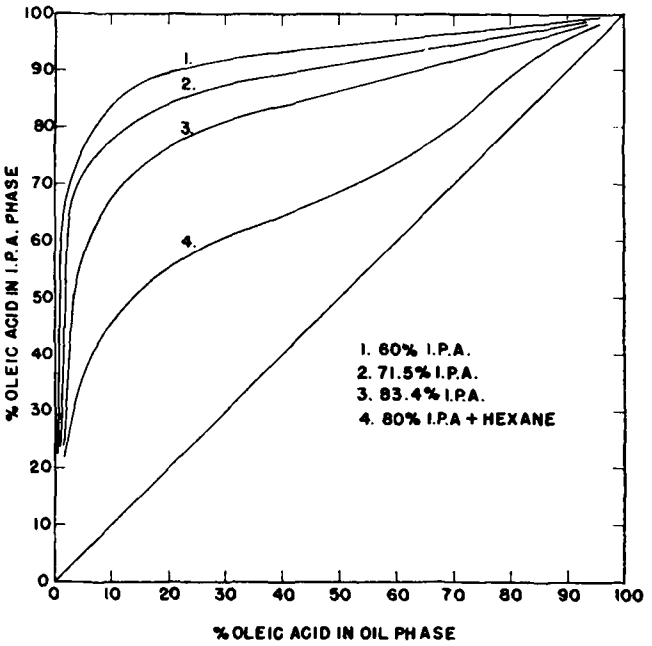


DISTRIBUTION OF OLEIC ACID BETWEEN ISOPROPANOL AND COTTONSEED OIL PHASES (SOLVENT FREE BASIS)

FIG. 2

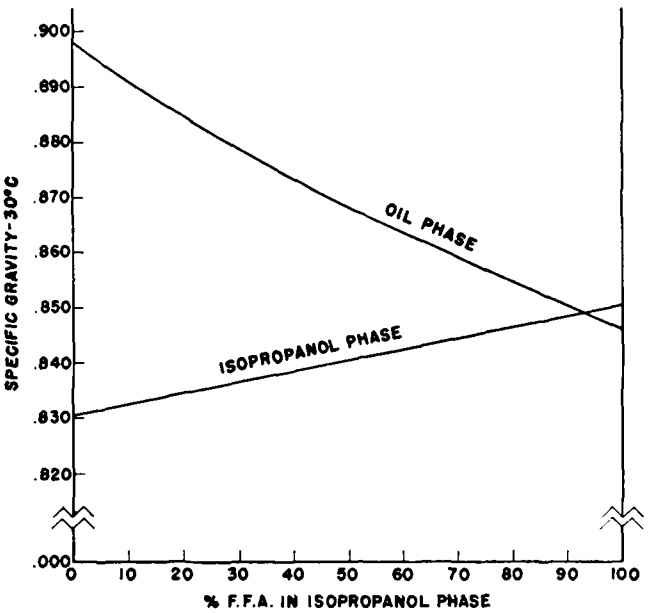
tion of fatty acid from oil lies between 70 and 80%. However the densities of the phases are also affected by fatty acid concentration and approach the same value when the acid in the isopropanol-water phase reaches 90% on a solvent free basis. The effect of fatty acid concentration on phase densities is shown in Fig. 3. When this system was used for liquid-liquid extraction, it was found impractical to enrich the fatty acids above 60% because of the slow rate of phase separation. Thus while the raffinate could be stripped of fatty acids, a small amount of oil would be lost in the extract.

The System: Hexane-Isopropanol-Water-Cottonseed Oil-Oleic Acid. In the liquid-liquid extraction process it was found advantageous to use a second solvent, hexane, to aid in separating the oil. Hexane introduced into the system dissolved preferentially in the oil phase and reduced its density to below that of the isopropanol-water phase. Hexane also lowered the viscosity of the oil phase and suppressed emulsification.

Solubility data for various mixtures of fatty acid and oil in hexane and 80% aqueous isopropanol are shown in Figures 4, 5, 6, and 7. In these diagrams the soluble regions are represented by areas in the upper left hand sides and lower right hand sides. In the extraction tests it was found that with isopropanol concentrations above 80% the mutual solubility of the phases was too great for practical operation. The distribution of oleic acid between the oil-hexane phase and isopropanol phase is shown in Fig. 2, Curve 4. For these determinations the composition of the mixture was 10% non-volatile matter, 20% hexane, 56% isopropanol, and 14% water. The per cent oleic acid in the non-volatile matter was varied between 0% and 100%. Although the distribution ratio is not as favorable as for the hexane free system, it is still very good. Variation in specific gravity for these equilibrium phases is shown in Fig. 8. The data show that this system may be utilized to separate efficiently oleic acid from cottonseed oil and the oil from the acid.

Liquid-Liquid Extraction Tests

The liquid-liquid extraction tests were made in a 2-inch I. D. glass column packed for 10 feet with ⅜-inch glass Raschig rings. A photograph of this column is shown in Fig. 9. The column was operated on a continuous basis with mixed miscella being fed into the center of the column, hexane being fed into the bottom of the column and water or dilute isopropanol fed into the top of the column. During operation of the column the hexane-oil phase moves up and the isopropanol-water phase moves down. In the top section the fatty acids and other dissolved impurities are stripped from the oil-hexane stream by the isopropanol-water phase. In the bottom section neutral oil is stripped from the isopropanol-water phase by hexane.



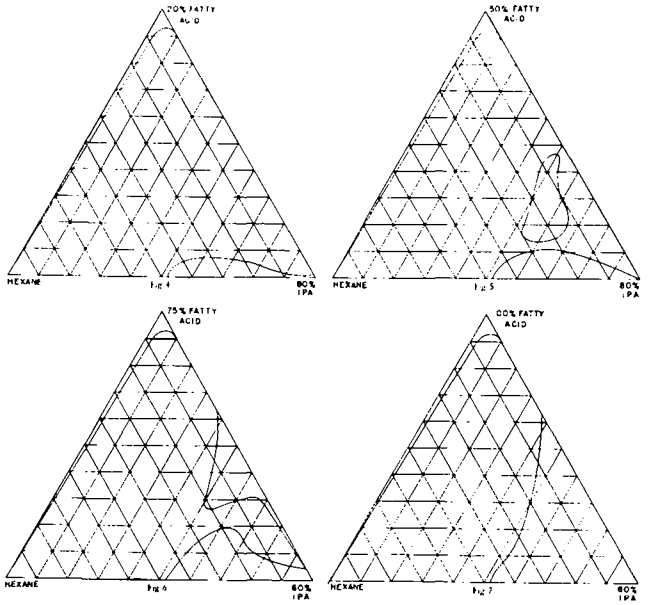
SPECIFIC GRAVITY OF PHASES IN EQUILIBRIUM

THE SYSTEM: OLEIC ACID-COTTONSEED OIL-ISOPROPYL ALCOHOL-WATER

FIG. 3

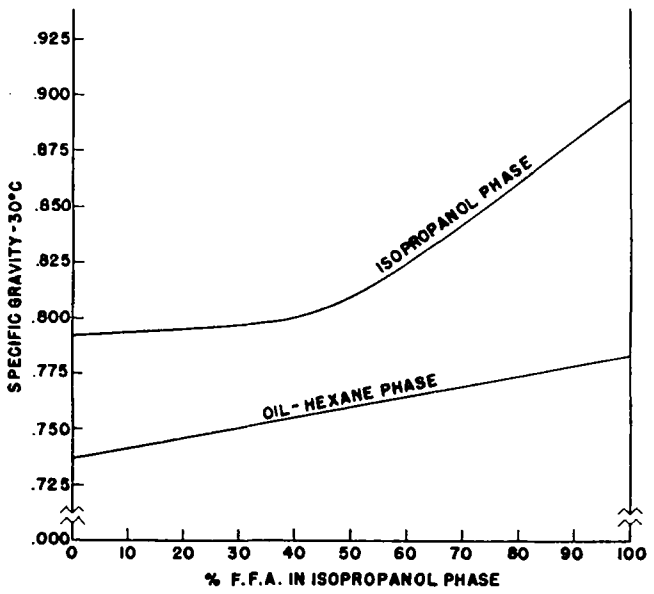
The best operating conditions for the extraction were found to be as follows: a miscella rate providing 1 lb. per hour of non-volatile material, fed to the center of the column; 1 to 2 lb. per hour of hexane, fed into the bottom of the column, and sufficient water or dilute alcohol, fed in the top to produce 10-12 lb. per hour of alcohol phase moving down the column. The feed rate was adjusted so that the concentration of alcohol in the column was 70%. The temperatures of feed streams were adjusted to give a column temperature of 30°C. Operating with the oil phase continuous gave the most satisfactory results.

Results of a typical liquid-liquid extraction run are given in Table I. In this run the miscella contained 9.95% non-volatile matter dissolved in 93 volume per cent isopropanol. The column feed rates were as follows: miscella 10 lb. per hour, hexane 1.8 lb. per hour, and water 2.6 lb. per hour. The oil-hexane raffinate contained 37% non-volatile material and



FIGS. 4, 5, 6, 7. Solubility curves for oleic acid-cottonseed oil mixtures in hexane and 80% isopropanol.

the isopropanol-water extract 0.70% non-volatile material. The analysis shows that the free fatty acid in the oil was reduced from 5.1% to 1.1% and the gossypol reduced from 1.0% to 0.2%. Other non-oil materials were reduced to an amount too small to measure accurately. The oil produced was dark in color. A sample of the oil from this run was evaporated to a volatile content of 0.6% and was refined in the laboratory using the standard slow break method for hydraulic cottonseed oil (5). The results were a refining loss of 3.2% and a refined color of 35 yellow and 5.2 red. The oil bleached (6) to a color of 20 yellow and 2.1 red. The soap stock produced was firm and did not yield any additional oil on reheating. Oil produced by this process appears to be very stable. Samples of it were stored for a period of six months without showing an appreciable increase in fatty acid content or developing a rancid odor or taste.



SPECIFIC GRAVITY OF PHASES IN EQUILIBRIUM

THE SYSTEM: OLEIC ACID-COTTONSEED OIL-ISOPROPYL ALCOHOL-WATER-HEXANE

FIG. 8

The isopropanol-water extract was analyzed in an attempt to determine the amount of neutral oil lost, but the quantity was too small for any accurate determination. The solvent-free extract appeared to meet the minimum requirements for merchantable soap stock (7).

Discussion

The Complete Extraction Process. A flow diagram of the process for the extraction of cottonseed oil

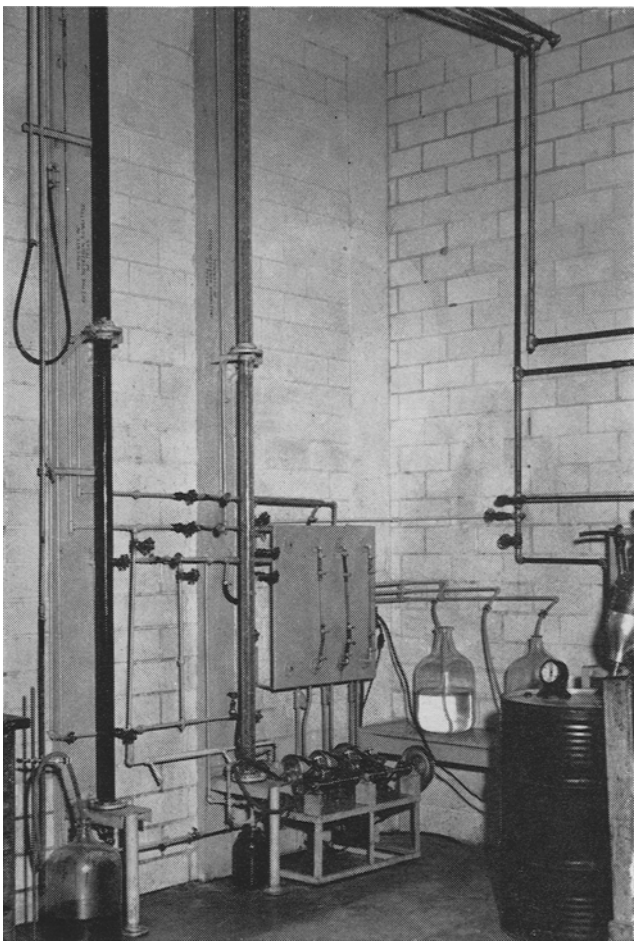


FIG. 9. Liquid-liquid extraction apparatus

with 91% isopropanol, separation of oil from the miscella by liquid-liquid extraction, and solvent recovery is shown in Fig. 10. In this process solvent economy may be attained by cooling the miscella to obtain phase separation and recycling a portion of the alcohol-water phase. This phase contains from 5-9% non-volatile matter of which about half is neutral oil. The remainder of this phase and the oil phase are fed to the liquid-liquid column. Raffinate emerging from the top of the column is stripped of hexane to recover the oil, and the hexane vapors are condensed and returned to the column. Extract from the bottom of the column contains about 5% hexane. This is evaporated, and the solvent vapors concentrated in a conventional rectification system. The small amount of hexane may be separated in a small azeotropic column, which can also be used to further concentrate isopropanol if desired.

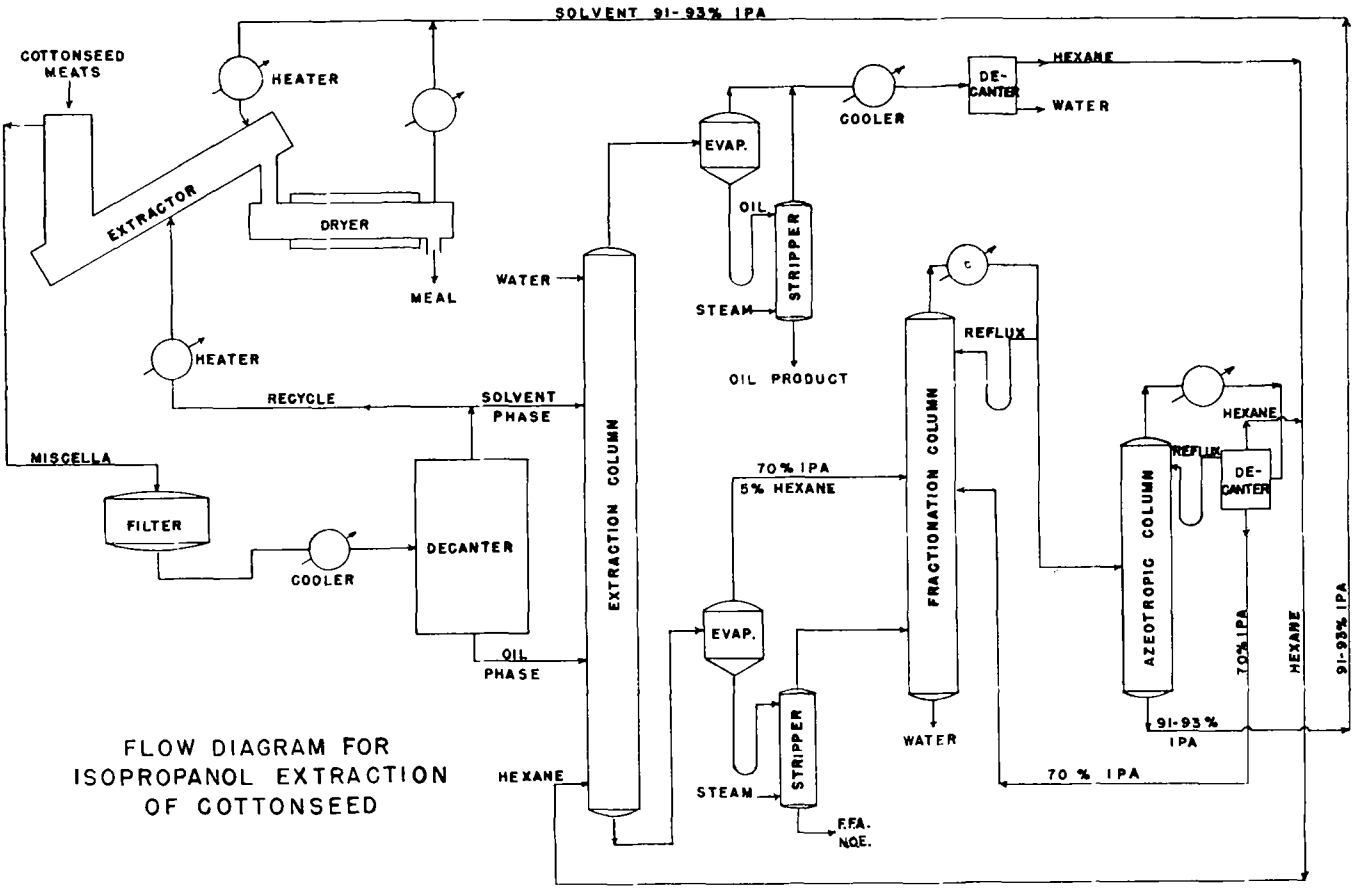


FIG. 10

The relative quantity of each stream will vary with the results desired and with the composition of the raw material fed to the extractor. If a meal, very low in both oil and gossypol is desired, the recycle stream to the extractor would be reduced and the total input of solvent increased. This in turn would result in a large quantity of dilute miscella being fed to the liquid-liquid extraction unit. In this case the top feed would be water in sufficient quantity to reduce the isopropanol:water ratio to the desired amount. If maximum heat economy is desired, the recycle stream from the decanter to the extractor would be increased. The resultant feed to the liquid-liquid extractor would contain a higher concentration of non-volatile material and the top feed would be dilute isopropanol-water solution in a quantity just sufficient to reduce the fatty acids and the non-oil materials in the neutral oil to the desired concentration. When meats from seeds having a high fatty acid content are extracted, the total quantity of the alcohol phase in the liquid-liquid extraction column would have to be increased to secure satisfactory separation. It has been found that the ratio of hexane feed to neutral oil feed in the liquid-liquid extraction column should be maintained in the range of 1:1 to 1:2. If the ratio is too low, the difference in the specific gravity of the two phases is too small to permit satisfactory operation of the column. If the ratio of hexane to neutral oil is too high, the fatty acids are extracted from the isopropanol phase and consequently the concentration of the fatty acids in the overhead is increased.

It is believed that the limit of this system has not been reached and that with more efficient equipment and a further study of the variables the liquid-liquid purification of the oil may be much improved.

Summary

It has been shown in the work reported previously (1, 2) that it is possible to extract the oil from cottonseed to produce gossypol-free meal of superior value. The miscella produced by this process contains the oil, free fatty acids, gossypol, and other non-oil materials. Solubility and distribution data have been established for the systems isopropanol-water-cottonseed oil and oleic acid and isopropanol-water-cottonseed oil-oleic acid-hexane. Using these data as a basis, a liquid-liquid extraction system has been developed which permits the separation of the miscella into a stable purified oil and a mixture of the free fatty acids, gossypol, phospholipids, sugars, and other non-oil materials. The process is sufficiently flexible to

TABLE I

Analysis of Run in Liquid-Liquid Extraction Column

	Feed[a] Miscella	Tops[a] Raffinate	Bottoms[a] Extract
	%	%	%
Neutral oil[b]	86.7	98.7	0.1
F.F.A.	5.1	1.1	35.0
(Non-oil extracts)			
Gossypol	1.0	.2	7.0
Phospholipids, Raffinose, Resins, Pigments[c]	7.2	<.1	58.0

[a] All analysis on solvent free basis. [b] By Wesson method. [c] By difference.

permit the extraction of cottonseed of variable free fatty acid content and to produce a product of controlled uniformity.

Acknowledgment

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Rapid Method of Copra Analysis and Its Application to the Various Oil Seeds

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THE analysis of copra presents a number of difficulties which must be overcome if dependable results are to be obtained. Most copra is highly variable in quality, such that in a sample sack, representing hundreds of tons, it would be difficult to find two pieces exactly alike. Spoilage, which causes the free fatty acids and color of the oil to be highest where the damage is most pronounced, sets in on the inner surface and progressively works outwardly toward the side which was attached to the shell. To make matters worse the fines, which are highest in free fatty acids and lowest in oil content (1, 2), must be uniformly incorporated in the sample in order that results may be consistent and reliable under any method of analysis. Pieces of coconut shell in the sample too must be reduced to small particles and likewise uniformly distributed.

Because of its high oil content copra cannot be ground by the ordinary laboratory mills without dislodging oil or otherwise rendering the sample unsuitable for all determinations. Nails, bolts, bottle caps, gravel, etc., are also a detriment for even under careful scrutiny these things occasionally slip through, further rendering laboratory mills unfit because they were not designed to handle such a mixture.

Considering the type of material and the tonnage it represents, the selected representative sample to be extracted must be large and its extraction complete, or very nearly so, in order that the results of the analysis may be reproducible and represent the quality of the lot as a whole. Extraction too must be cold and rapid to prevent any possible change in the free fatty acids and color of the oil during an otherwise hot and prolonged extraction. Rapidity, simplicity, and a minimum of manipulation are also desirable for many reasons, such as accuracy, time saving, and the prompt availability of results when they are quickly needed.

All the above problems have been successfully solved by the new method, made possible by the development of new equipment and some improvements on other heretofore in use. Among other things the method employs a specially equipped blender, or mixer for the trituration of the material and extraction of the oil by means of a suitable solvent, and the removal of the solvent from the oil by the application of heat and vacuum simultaneously. Further details will be given later in conjunction with the various steps of the procedure. The use of a mixer for the extraction of oil from oil seeds in the presence of a solvent is not new. We began using the Whiz-Mix blender for this purpose in 1941 and in the intervening time various publications have reported the use of the Waring Blendor in oil and fat extraction (3, 4, 5, 6).

Although the extraction of samples, large or small, is rapid by the new method, total extraction is more nearly complete in 10 minutes than it is with one of the best extractors, now in use, in an eight-hour period. We have run numerous samples by the *Goldfisch Method* and the *Rapid Method* for comparison and in all cases extraction was best by the latter method in spite of the fact that samples 15 times larger were used and time of extraction only 10 minutes instead of eight hours by the former method. Results are shown in Table I.

Comparison with the Soxhlet, Smalley, and Butt extractors was not obtained because these extractors are known to be slower than the Goldfisch extractor. In a 21-hour extraction period however the Soxhlet and the Butt compared favorably with the latter extractor (7).

The better results obtained by the new method of course are based on the fact that no channeling is possible on account of the vigorous agitation and the copra meal becomes so fine by the trituration that, after filtering, washing with solvent, and drying, it can pass through a No. 100 sieve.

The rapidity of the method makes it possible for a chemist, after the copra is chopped, to turn out the complete analysis of a sample, comprising moisture, oil content, color, and free fatty acid determinations in two hours, and if there are several samples to be run together, the time consumed per sample is reduced to about one hour.

The method also makes possible the extraction of large amounts of oil, such as four-ounce bottles, to be sent to interested parties before actual crushing takes place. The method is likewise suitable for the rapid extraction of expeller cake. Results have been compared with those obtained with the Goldfisch extractor and are shown in Table II.

Since the equipment used is in large part new, a brief description thereof will be presented to familiarize the reader before passing on to the analytical procedure.

The Copra Chopper. This chopper, shown in Figures 1 and 2, is a machine similar to a hammer mill, but instead of hammers it has fixed steel blades, the cutting edges of which have been made extremely