additives [illegible] tend to give fluid or very slow-draining films [illegible] suggested from the available data.

a) In general it appears that aqueous solutions of pure detergents give fluid films which show relatively fast drainage rates.

b) Some detergents to which certain types of organic polar compounds are added give very slow-draining films. Such detergents generally contain a normal saturated hydrocarbon chain of at least 12 carbon atoms with a hydrophilic group in the terminal or in the beta position. Examples are soaps (sodium salts of long straight chain fatty acids), sodium normal primary alcohol sulfates as well as the sodium paraffin 2-ol sulfates.

c) The organic polar additives which tend to give slow-draining films have essentially similar hydrophobic structural characteristics to the detergents described in b) above. However they are relatively insoluble in water and in the presence of detergent may form non-gaseous (condensed) types of surface films which have high surface viscosity. Most of these additives however are probably solubilized by the detergent solution. It is postulated that the extent of solubilization should not be so great as to interfere with adsorption at the air-liquid interface (film or foam). Typical examples are fatty acids and long straight chain primary alcohols as well as 1,2-diols.

d) On the other hand, there are some types of detergents which apparently give fluid films when the above organic additives are present. In these cases the hydrophobic part of the detergent may have a highly branched chain, a cyclic structure, or unsaturated groups (cis form). Examples are sodium secondary alcohol sulfates where the sulfate group is further from the end of the chain than the beta position, sodium alkyl aryl sulfonates, and sodium salt of oleyl derivative of methyl taurine.

e) A variety of organic additives do not give slow-draining films when added to solutions of detergents described under b), and these additives have similar structural characteristics to the detergents described under d). When no polar group is present in the additive, the film remains fluid. Saturated and unsaturated hydrocarbons are typical examples. Cyclic alcohols (hydroabietic and lanolin alcohols) do not form slow draining films and among the unsaturated primary alcohols, oleyl alcohol has no effect, but elaidyl alcohol does tend to slow down film drainage. This again shows that unsaturated compounds (of the cis form) do not give slow-draining films.

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Isopropanol as a Solvent for Extraction of Cottonseed Oil* III. The Use of Recycling to Effect Solvent Economy[1]

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EXTRACTION of oil and other substances from cottonseed meats with isopropanol has been shown to produce a meal of superior nutritive value for swine as compared with the average meal obtained by hydraulic methods. When isopropanol was used to extract the oil, free gossypol in the meal was reduced to a safe level for consumption by single-stomached animals (1). Subsequent tests show that the meal may be safely fed to laying hens without lowering productivity or causing the stored eggs to become off-color.

Since isopropanol extracts gossypol and other compounds as well as oil from the meal, the extracted matter may contain as high as 10 to 15% non-oil material. This material includes significant quantities of carbohydrates, gossypol, and resinous substances related to gossypol in addition to the fatty acids, phosphatides, and sterols normally occurring in crude oil. In previous work a study of the phase relationships of oil and other substances in aqueous isopropanol has shown that the oil may be separated from the miscella substantially free of impurities (2). Liquid-liquid extraction principles may be used to improve the efficiency of this separation and prevent loss of oil with the impurities.

Although isopropanol has many advantages as a solvent for extraction of vegetable oils, it has several serious disadvantages. The latent heat of vaporization is nearly double that of hexane. In addition, it forms a constant boiling mixture with water at 91% by volume. To obtain higher concentrations, a special process, such as azeotropic distillation is required; therefore it is desirable to use 91% isopropanol for extractions. On the other hand, 91% isopropanol has a low solvent capacity for oil, and the miscella is limited to about 10% extractables. This requires a high solvent-to-meats ratio which, when combined with the high latent heat, causes steam requirements for the process to be high.

To reduce heat requirements, acetone was considered as a substitute for isopropanol and was tested in parallel extraction runs. Acetone has a low latent heat and can readily be concentrated by simple rectification. Its disadvantages are a considerably greater fire hazard, though not greater than hexane, and somewhat higher cost.

The primary objective of this work was to determine the advantages which might be obtained by cooling the miscella to separate a solvent phase from the oil and recycling this phase back through the rich end of the extractor. This principle has previously been tried with ethanol and mixtures of ethanol and isopropanol (3, 4). However it was desired to determine the effect of recycling on fresh solvent requirements and extraction efficiency as well as on the products, oil and meal.

Procedure

Examination of the solubility curves for isopropanol-water-cottonseed oil at 30°C. and 70°C. (Figure 1) shows a high increase in oil solubility with a concurrent temperature rise for 91% isopropanol.

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This is indicated by the dotted line originating at 91% isopropanol. Similarly in Figure 2, the oil solubility shows a maximum variation with temperature when dissolved in 95% acetone. For these reasons 91% isopropanol and 95% acetone were used in the recycle extraction tests.

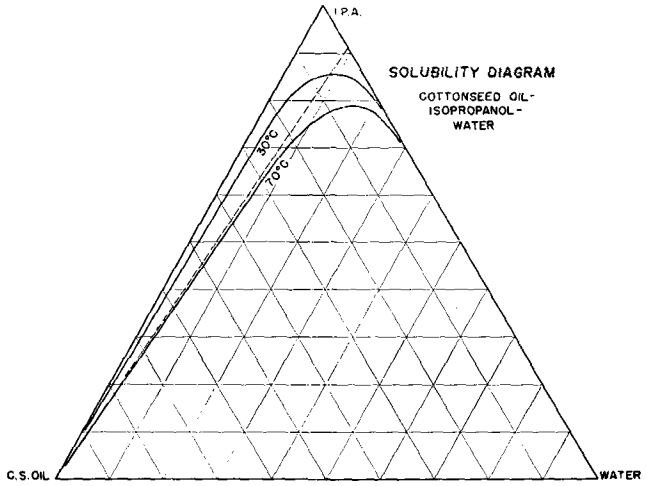

FIG. 1.

Extractions were conducted in a small continuous, countercurrent, screw extractor which has been described in an earlier paper (1). Runs were made with isopropanol and acetone, using both straight extraction and recycling. Data were also obtained for a straight extraction run with hexane for comparison. All runs were conducted for a period long enough to assure constant operating conditions.

A flow diagram (Figure 3) shows the arrangement for recycling the solvent phase of the miscella. The hot miscella was cooled in an exchanger to 80-85°F. and the phases continuously separated in a five-gallon glass bottle. The top or solvent layer was pumped through a flowmeter, then a reheater, and back into the approximate center of the extraction section.

Cottonseed meats were prepared for the tests by adjusting the moisture to approximately 10% and then rolling to about 0.006-inch flakes in flaking rolls. The meats feed rate for all runs was 10 pounds per hour, which gave an estimated residence time of approximately 1.25 hours. Extraction temperatures were 70°C. for isopropanol and 50°C. for acetone, and a high solvent recycle rate of 60 pounds per hour was maintained since this favored extraction.

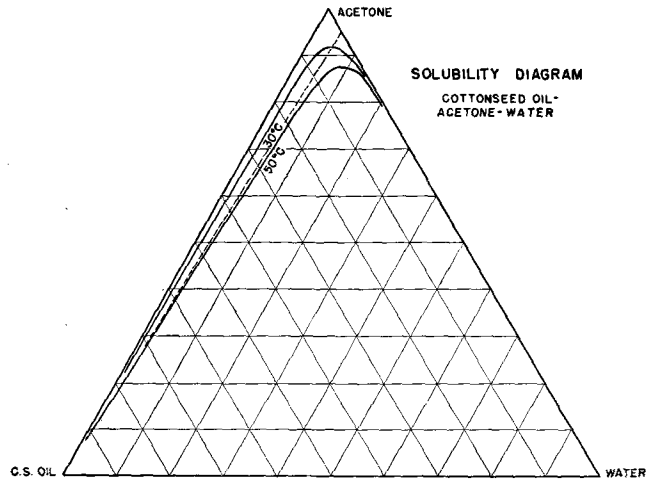

FIG. 2.

The minimum feed rate of fresh solvent was determined by decreasing the flow in increments until the oil content of the meal was increased. The increase was very sharp below a solvent-to-meats ratio of 1:1.

A comparison of solvent requirements for extraction runs, using isopropanol and acetone with and without recycle, is shown in Table I. The residual oil in the meal for these runs was below 1.0% except the recycle acetone run. Here the fresh solvent rate was slightly below the minimum feasible value, and the residual oil in the meal was 2.8%. Actually no excess solvent phase was produced in this run and only an oil phase of 65% oil was removed as product.

TABLE I

Solvent and Heat Requirements for Various Cottonseed Oil Extraction Methods

	Hexane	93% I.P.A. Straight Run	91% I.P.A. Recycle	95% Acetone Straight Run	95% Acetone Recycle
Ratio, solvent/meat	1.64:1	3:1	1:1	3:1	0.9:1
Solvent to dryer, lb./lb. meats	0.68	0.68	0.67	0.67	0.73
Solvent in miscella, lb./lb. meats	1.32	2.32	0.33	2.32	0.17
Calculated steam, lb./lb. meats	0.30	1.04	0.36	0.77	0.23

The quantity of solvent retained by the meal entering the dryer was the same in all cases except for the recycle acetone run. The heat required for preheating fresh solvent and recycle solvent was not included since this could be obtained from solvent vapors. This would also save cooling water.

Calculations for steam requirements were made only for heating and evaporating solvent in the dryer and from the miscella. Heat requirements for the recycle runs are shown to be comparable to straight extraction with hexane.

Portions of the oil phases separated from the isopropanol and acetone miscellas were countercurrently extracted with fresh solvent in a small glass column. The purpose was to observe to what extent the refining loss could be reduced by a more efficient separation of impurities having greater solubility in the solvent phase than the oil. All of the oils produced were stripped free of solvent, refined by the standard cup method, and bleached. The results are shown in Table II.

These figures show considerably lower losses for the alcohol- and acetone-extracted oils, particularly those which had been washed with fresh solvent. The higher colors shown by some samples are at least partly due to lack of enough oil to determine proper refining concentrations rather than poor oil quality.

Analyses for the meals are shown in Table III. The high free gossypol content of the hexane meal is due to the fact that it had not been heated or cooked. The hexane-extracted meal was lightest in color while the recycle meals were darkest. There is evidence that considerable gossypol is bound in some form, in the recycle meals, rather than extracted.

TABLE II

Refining Losses and Color of Extracted Cottonseed Oils

	Method of Preparation						
	Hexane Extracted	93% I.P.A. Straight Run L-L Treated	91% I.P.A. Recycle Extracted Oil Layer	91% I.P.A. Recycle L-L Treated with 70% I.P.A.*	91% I.P.A. Recycle L-L Treated with 70% I.P.A. and Hexane*	95% Acetone Extracted Oil Layer	95% Acetone Extracted Oil Layer L-L Treated 90% Acetone*
Free fatty acid	2.0	1.3	1.3	.53	.65	1.1	0.16
Refining loss	8.5	3.0	5.0	3.6	4.0	5.0	3.5
Refined color	4.4	5.5	5.2	4.5	5.0	5.2	3.4
Bleached color	1.8	2.6	2.0	1.5	2.1	2.9	1.7

All analyses according to A.O.C.S. methods.

* For Extraction Procedure see Harris and Hayward, J.A.O.C., *26*, 719-723 (1949).

Discussion

In recycling the solvent phase back through the extractor the impurities tend to build up in this phase. In general, this tends to decrease the solubility of the oil; however, with seed containing a high percentage of free fatty acids the solubility of the oil in the solvent phase may be increased.

TABLE III

Comparison of Cottonseed Meals Classified by Extraction Method

	Hexane	93% I.P.A.	95% Acetone	91% I.P.A. Recycle	95% Acetone Recycle
Per cent moisture	10.0	10.2	7.8	11.0	10.7
Per cent oil	0.57	0.92	0.95	0.59	2.80
Per cent gossypol	0.98	0.010	0.033	0.019	0.060

The moisture content of the meats fed to the extractor was approximately in equilibrium with 91% isopropanol and only slightly above equilibrium with 95% acetone. For this reason, water content of the solvent changed only slightly during extraction. Most of the water in the meats is carried into the dryer where some was driven off with the solvent and some remained with the meal. The dryer condensate contained about 2.0% more water than fresh solvent, while the solvent recovered from the miscella had been diluted less than 1.0%. Volatile matter in the meals ran from 8 to 11%, and this was believed to be essentially water since they were free of solvent odor.

A solvent-to-meats ratio of 1:1 produces some solvent phase as product in addition to the oil phase. This may be termed a "bleed stream" since it is rich in impurities including fatty acids, phospholipids, and sterols normally occurring in crude oils. After solvent evaporation, the nonvolatile matter could be sold as soapstock, or utilized for by-product recovery. The amount of oil lost in this "bleed stream" is dependent on the quantity of solvent phase produced and on the fatty acid content of the seed.

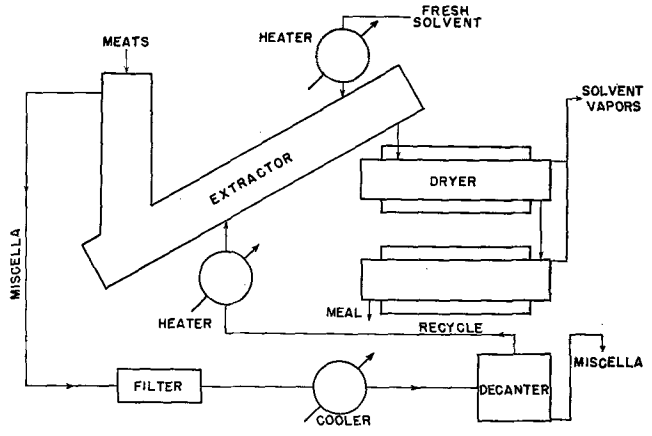

FIG. 3.

TABLE IV

Distribution of Oil 91% Isopropanol Extraction of Cottonseed Using Recycle

	Products [a]			
	Meats	Meal	Solvent Layer Miscella (Top)	Oil Layer Miscella (Bottom)
Pounds oil	24.31	.41	1.33[b]	24.11[b,c]
Pounds F.F.A.	.55	.01	.34	.20

[a] Basis: 100 lb. meats containing 8 per cent moisture, 24.86 per cent oil, 4.5 per cent fatty acids, by A.O.C.S. Analysis.

[b] Includes non-oil materials exclusive of fatty acids.

[c] Refining loss 5 per cent.

An "oil balance" for the recycle isopropanol run is presented in Table IV. This is based on a material balance for eight hours of constant operation. The totals for the meats and meal columns were obtained by petroleum ether extractions of the samples, and the totals of the solvent layer and oil layer columns were calculated from the nonvolatile matter in these products. The actual neutral oil in the solvent layer could not be determined by the Wesson method, and a material balance shows it to be very small. A summary of this table shows that of 24.86 pounds of petroleum ether soluble oil and free fatty acids extracted from 100 pounds of meats, 24.31 pounds were obtained as crude oil. Based on the A.O.C.S. refining loss method, 23.1 pounds of prime grade refined oil would be obtained. This represents a yield of edible product amounting to 92.9% of the original oil in the meats.

The results of this work show that it is possible to use a partially miscible solvent, such as acetone or isopropanol, with recycling to effect considerable solvent economy. The use of a water and oil miscible solvent such as isopropanol or acetone will permit reduction of free gossypol in the meal and an efficient recovery of neutral oil.

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