Isopropanol as a Solvent for Extraction of Cottonseed Oil

I. Preliminary Investigations

W. D. HARRIS,[1] F. F. BISHOP,[1] C. M. LYMAN,[2] and R. HELPERT [1]

Introduction

THE application of solvent extraction methods has met with considerable success in the soybean industry. In the past few years economic conditions in the cottonseed industry have favored the development of extraction process and several plants have been, or are being, constructed. However, the structure of cottonseed is considerably different from that of soybeans, and its processing is complicated by the presence of the gossypol group of compounds. There is also a tendency for the cottonseed meat particles to disintegrate during extraction to produce an undesirable quantity of very fine particles. Commercial petroleum solvents, which are standard for soybean and other oil seed extractions, leave most of the gossypol in the meal. However, there is a small portion of this substance extracted along with the oil which may become altered during evaporation of the solvent to give a "fixed" red color in the oil (1). Gossypol has been shown to exert a toxic action on certain animals. According to Mosgov (2) 3 mg. of gossypol in olive oil per kilogram of body weight is toxic to dogs, rabbits, and young swine. In the hydraulic process for cottonseed, gossypol is partially decomposed by cooking. Lyman (3) has shown that it is necessary to cook moistened cottonseed 90 min. at 122° C. to reduce the effect of gossypol on growth rates of guinea pigs. His work further indicates that this degree of cooking reduces the active gossypol content of the meal to approximately 0.02%. Recently Boatner and co-workers (4) have observed the effect of cooking on conversion of gossypol to gossycaerulin and gossypurpurin.

When raw cottonseed is solvent extracted with petroleum solvents, the meal must be cooked excessively to render the gossypol inactive. Results obtained in this research indicate that the ill effects of gossypol might better be alleviated by some other method than thermal decomposition. Residual gossypol pigments and denatured proteins render highly cooked meal unsuitable as a source of commercial protein. It has also been demonstrated by Olcott (5) that cooking lowers its nutritional value.

Cottonseed meats contain a number of chemical substances which are present in sufficient quantities and have such properties that they would have an increased value as separate pure products. These are: protein, oil, fatty acids, phospholipids, gossypol, and sugars. Other substances such as the tocopherols and sterols, although in lesser concentration, are also possible products of value. A goal in cottonseed processing could well be the separation of these substances in purified form for commercial use. Complete exploitation of the possibilities of solvent extraction may make possible the attainment of this goal.

[1] Chemical Engineering Department, A. & M. College of Texas.
[2] Texas Agricultural Experiment Station, A. & M. College of Texas.

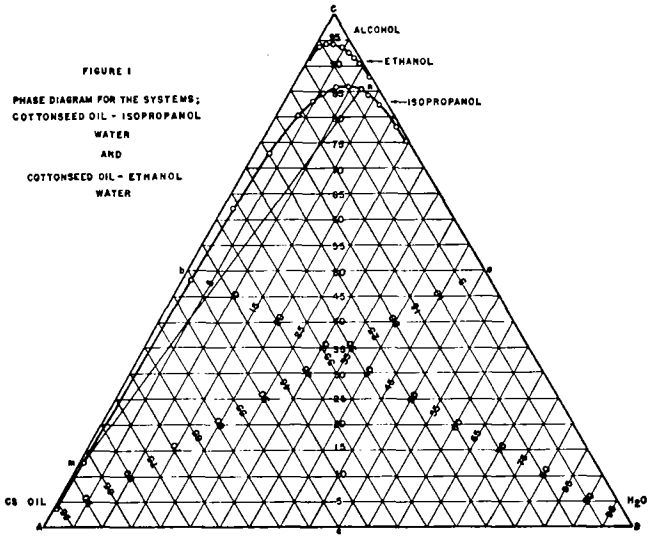


FIGURE 1
PHASE DIAGRAM FOR THE SYSTEMS; COTTONSEED OIL - ISOPROPANOL WATER AND COTTONSEED OIL - ETHANOL WATER

This report describes investigations in which isopropanol and mixtures of isopropanol with hexane were used to extract gossypol and other substances, as well as oil, from cottonseed meats. Liquid-liquid extraction methods were found applicable for separating oil and fatty acid fractions from the miscella, and feeding tests on the raw extracted meal showed it to have a markedly superior nutritive value to commercial hydraulic meal.

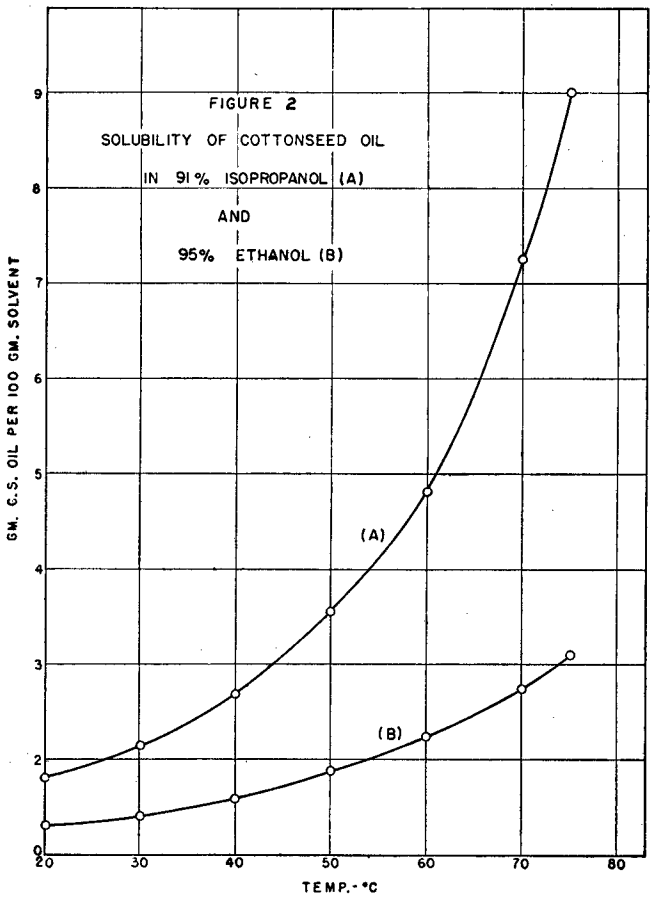
Solvent Properties of Isopropanol

Since cottonseed oil is not completely miscible in aqueous isopropanol, information on solubility and phase equilibria is necessary. At equilibrium, the alcohol is distributed between the immiscible substances, oil and water. These phases will be called the oil phase and the water phase.

Solubility data for the system cottonseed oil-isopropanol-water were determined by a cloud point method, which proved to be the simplest and most accurate of several methods tried. In this method, water was added from a burrette to weighed quantities of oil and alcohol until a permanent cloudiness developed. The titration was conducted in a closed, three-necked flask equipped with a thermometer, stirrer, and microburrette. The flask was immersed in a constant temperature bath. Purified isopropanol, obtained by fractionating commercial 99% alcohol with a Stedman column, and caustic refined, hydraulic cottonseed oil were used in the determinations.

Phase equilibrium data were obtained by analyzing the layers which separated at constant temperature from mixtures of the three components. Oil content of the layers was obtained by evaporation of alcohol and water, and the percentages of the latter were then obtained from solubility data.

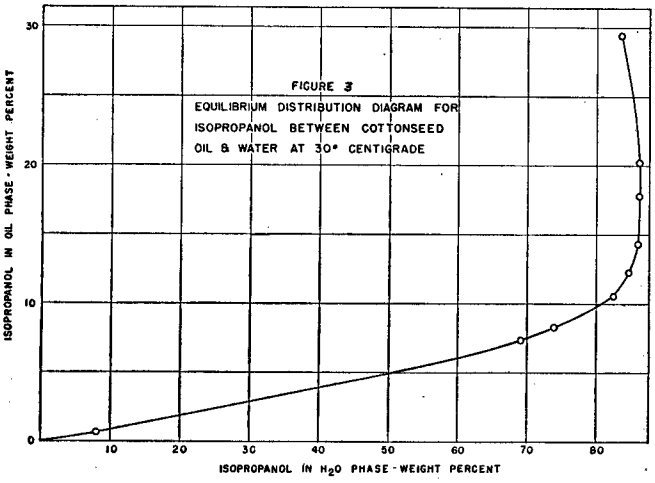
The ternary phase equilibrium diagram for 30° C. is shown in Figure 1. For comparison, the curve for



ethanol is also shown. It is evident that ethanol oil mixtures have a much lower tolerance for water.

The tie line, mn, shows approximately the composition of an oil phase in equilibrium with a saturated solution of oil in 91% isopropanol. The values, 87% oil and 2.5% oil, for the two phases agree very well with the concentrations in layers which separate from a cottonseed oil miscella when 91% isopropanol is used as solvent. However, the presence of fatty acids will increase oil concentration in the water phase.

Figure 2 shows the effect of temperature on solubility of oil in 91% isopropanol and 95% ethanol. These concentrations are the constant boiling mixtures with water. By extrapolation of this curve, 91% isopropanol is estimated, to dissolve approximately 12% oil at its boiling point, 80° C. The phase distribution curve, Figure 3, for alcohol, between oil and water, shows that the alcohol is considerably more soluble in the water phase. This ratio of alcohol concentration in the water phase to that in the oil phase varies from 13.3 at low concentrations to 2.6 for 30% alcohol in the oil phase. On the basis of these results, it was found possible to remove the alcohol from oil by countercurrent extraction with a very small amount of water.



Distribution of Fatty Acids

The use of isopropanol for separation of fatty acids from glycerides has been suggested by Van Dijeck (7). In extraction tests on cottonseed, it was noticed that the oil phase which separated from the miscella was lower in fatty acids than the seed analysis showed. Accordingly, tests were made to determine the relative phase distribution of fatty acids and cottonseed oil in isopropanol-water mixtures. In these tests, crude hydraulic cottonseed oil containing 1.25% fatty acid was used and equilibrium conditions were obtained at 30° C. Table I shows the effect of varying water content on the phase distribution of fatty acids. The data show that high water concentration in the system favors separation of fatty acids from oil, however, in runs 5 to 8 the phases separated very slowly. Fatty acid concentration in the oil phase was at a minimum in runs 4 and 5.

The equilibrium distribution of fatty acids, as a function of their concentration, is shown in the curve, Figure 4. In this case the system composition was: oil plus fatty acids, 20 parts; isopropanol, 80 parts; and water, 10 parts by weight. The temperature was 30° C. and the fatty acid content is expressed on a solvent free basis.

Gossypol Extraction

Gossypol and its related compounds are readily soluble in aqueous isopropanol. When cottonseed meats

TABLE I.

Phase Distribution of Cottonseed Oil and Fatty Acids in Isopropanol-Oil-Water Mixtures.[1]

Run	Composition of the system			Phase analysis							
				Bottom layer				Top layer			
	Oil, gm.	Isopropanol (99%) gm.	H_2O, gm.	Rel. vol., %	Sp. gr.	Oil, %	F.F.A.,[2] %	Rel. vol., %	Sp. gr.	Oil, %	F.F.A.,[2] %
1	20	80	2.5	10.0	.8650	71.4	0.4	90.0	.8060	14.6	1.63
2	20	80	5.0	15.1	.8770	78.2	0.45	84.9	.8061	7.8	3.07
3	20	80	7.5	16.6	.8836	82.6	0.3	83.4	.8110	4.52	5.1
4	20	80	10.0	16.3	.8871	85.5	0.2	83.7	.8135	3.06	7.48
5	20	80	12.5	14.4	.8900	87.0	0.2	85.6	.8230	2.1	10.6
6	20	80	15.0	12.0	.8903	87.5	0.3	88.0	.8272	1.67	12.6
7	20	80	20.0	13.0	.8925	88.6	0.4	87.0	.8381	1.07	17.75
8	20	80	25.0	13.5	.8947	90.2	0.4	86.5	.8515	0.8	21.0

[1] Temperature 30° C. [2] Solvent-free basis.

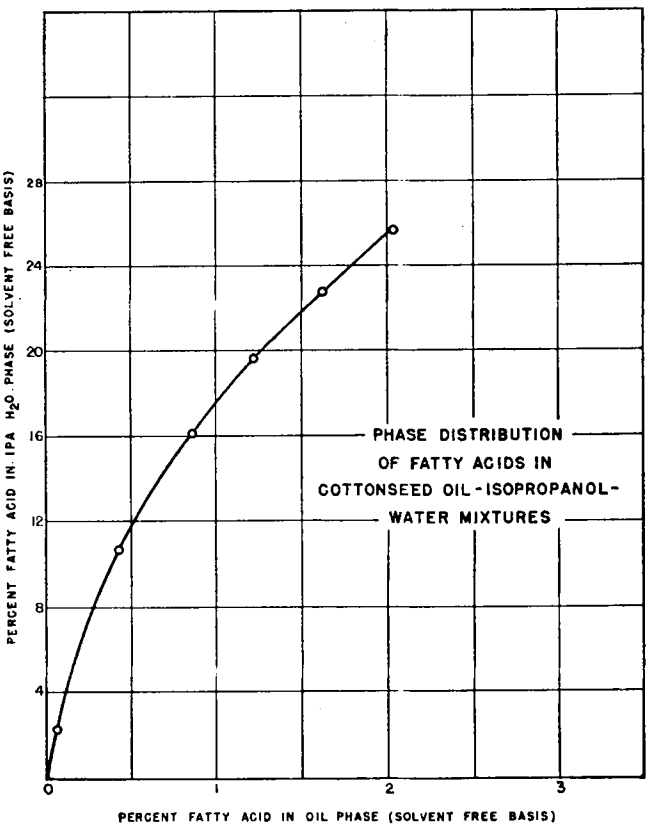


FIG. 4.

are extracted with 91% isopropanol under conditions suitable for removing the oil, gossypol is also removed. A comparison of the rates of gossypol extraction by several mixtures of isopropanol and water and 91% isopropanol plus hexane is shown in Table II.

TABLE II.

Extraction of Gossypol From Cottonseed Flakes by Isopropanol Mixtures.*

Run	Solvent	Gossypol extracted % of total
1	99% Isopropanol	31.2
2	91% Isopropanol	78.0
3	50% Isopropanol	89.8
4	90% Isopropanol 10% Hexane	97.4
5	50% Isopropanol 50% Hexane	98.8
6	10% Isopropanol 90% Hexane	93.1

* Flakes contained 0.676% gossypol.

These results were obtained by shaking 0.2500 g. samples of ground meats with 100 ml. of solvent for one hour and analyzing aliquot portions of the extract. The analyses were made by the gossypol-aniline spectrophotometric method as recommended by Smith (8). Although these data indicate that hexane-isopropanol mixtures should be valuable for extracting gossypol, this was not born out in pilot plant extractions. The inconsistency will be discussed later.

Raffinose

When cottonseed meats were extracted with hot 91% isopropanol and the miscella allowed to cool, considerable quantities of sugar crystallized out. The sugar was purified by recrystallization and identified as raffinose, a trisaccharide. It is not very sweet and has no commercial value at present. With complete hydrolysis, raffinose splits to give a molecule each of glucose, fructose, and galactose (6). Isopropanol concentrations higher than 91% and mixtures of isopropanol with hexane do not extract appreciable quantities of this sugar.

The gossypol compounds, phosphatides, and sugars are the main impurities in the isopropanol-cottonseed miscella. When the miscella is split into two phases, essentially all of these impurities pass into the water phase leaving the oil phase quite pure.

Pilot Plant Extractions

Pilot plant extractions were made in a small continuous extractor of the screw type. Figure 5 shows a schematic diagram of this extractor. Three 4-inch screw sections in series carry the meats down through the solvent, then up out of the solvent and through a jacketed drying section. Solvent is preheated and fed into the vertical screw, whence it flows downward by gravity, countercurrent to the flow of meats. The extraction section was wrapped with a copper tube carrying steam and insulated to maintain the desired temperature.

Extractions were made with commercial 91% isopropanol, 99% isopropanol, and mixtures of isopropanol with a petroleum solvent. The petroleum solvent had a boiling range of 152° F. to 156° F. and is known as commercial normal hexane. It will be referred to as hexane. Cottonseed flakes, varying from 0.005 inches to 0.008 inches in thickness were prepared by hulling and flaking with standard mill room equipment. It was found necessary to increase the moisture content of the meats to 10-12%, before flaking, since at low

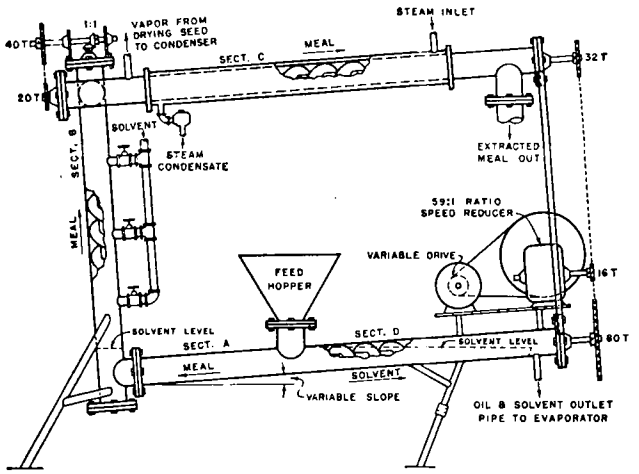


DIAGRAM OF EXPERIMENTAL CONTINUOUS SOLVENT EXTRACTION APPARATUS

FIG. 5.

moisture content the solvent would not percolate through the meats. High moisture content in the meats proved to be beneficial in three other ways: better flakes were produced by the rolls, occurrence of fines in the miscella and in the dryer was almost eliminated, and extraction of gossypol was improved.

When 91% isopropanol was used, it was found advisable to preheat the solvent to 170° or above and to maintain at least 160° F. in the extraction section. Lower temperatures caused the separation of a heavy oil layer which was carried back along with the meats. The extractor operated very satisfactorily, and test runs up to 15 hours' duration were made. The combination of high moisture in the meats with 91%

isopropanol caused fine meat particles to coagulate during extraction and settle readily so that the miscella emerged perfectly clear. Advantage of the coagulating tendency was also obtained in the meal dryer. No dust was produced, and the meal came out in granular form.

TABLE III.

Typical Analysis of Cottonseed Extraction Run With 91% Isopropanol.

	lb./hr.
Cottonseed flakes feed rate	6
Solvent feed rate	31.1
Meal rate	3.8
Miscella rate	23.8
Recovered solvent from dryer	6.5
Flake analysis	per cent
Moisture	9.2
Oil (N. C. P. A. method)	30.4
Isopropanol soluble	37.3
Protein	32.0
Gossypol	0.775
Meat analysis	
Moisture	3.5
Oil (N. C. P. A. method)	0.3
Isopropanol soluble	4.1
Protein	58.8
Protein solubility (3% NaCl)	67.5
Gossypol	0.0108
Miscella (combined layers)	
Oil (non-volatile)	7.6
Top layer	
Non-volatile	3.3
Fatty acid (solvent free basis)	6.3
Bottom layer	
Oil	87.0
Fatty acid (solvent free basis)	0.06

The summary of a typical extraction run is shown in Table III. In these runs a fairly high solvent to meats ratio was maintained in order to obtain a highly extracted meal for feeding tests. Protein solubility tests were made to determine the denaturing effect of the alcohol. The values obtained are not appreciably lower than those for meal extracted by hexane in a similar manner.

Extractions with 99% isopropanol gave a very light meal but did not remove as much of the free gossypol. This concentration dehydrated the meats so that disintegration occurred with some resulting fines. The optimum concentration appears to be between 91% and 99% isopropanol.

Mixtures of hexane and isopropanol were not as efficient for reducing gossypol. A 50% by wt. mixture of hexane and isopropanol left 0.05% free gossypol in the meal while, with the same operating conditions, 91% isopropanol left 0.011% gossypol in the meal. These results are not in agreement with data shown in Table II, and an explanation may be in the low affinity of the hexane mixture for water. The cottonseed meats tend to absorb considerable water and alcohol in preference to the hexane and carry it into the dryer. Gossypol, being more soluble in the water-alcohol mixture, will also stay with the meats.

Meal Feeding Tests

The nutritive value of 91% isopropanol extracted meal was compared with four prime grade hydraulic cottonseed meals by rat feeding tests. The results are shown in Table IV. Since this test was devised to emphasize differences in protein quality, the ration was limited to 12.0% protein which was supplied essentially by the test meal.

This meal has also been tested in feeding swine. As the sole protein supplement, it gave equally as good results in gain and efficiency of gain as soybean meal and a number of different samples of meat scraps. The gains were substantially greater than obtained on hydraulic cottonseed meals. Isopropanol extracted

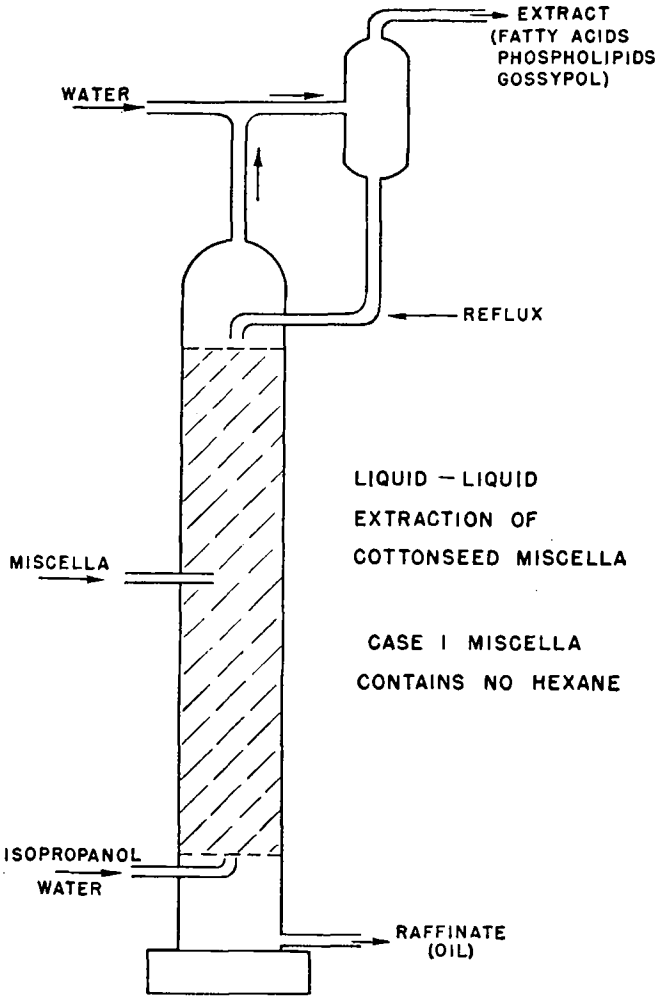


FIG. 6.

meal may be fed free choice to young pigs, which is not possible with most hydraulic meals. Data on swine and chicken feeding tests will appear in a subsequent paper.

Miscella Recovery

The miscella obtained by extraction of 100 lb. of cottonseed meats with 91% isopropanol contains approximately 31 lb. of oil substances and 4 lb. of non-

TABLE IV.

Comparison of Hydraulic and Isopropanol Extracted Cottonseed Meals in Rat Feeding Tests *

Type of meal	Average gain in wt.**
	gm.
Hydraulic Meal No. 1	37.4
Hydraulic Meal No. 2	37.6
Hydraulic Meal No. 3	27.8
Hydraulic Meal No. 4	34.7
Isopropanol extracted	72.2

* Protein was limited to 12%and was essentially all supplied by test meal.

** Groups contained 6 rats.

oil compounds. Evaporation of the solvent gave a very dark oil with considerable foots. However, when the oil phase which separated from the miscella was washed with water to remove the alcohol, and caustic refined, a prime grade oil was obtained.

By using oil solubility data and assuming the miscella to contain 10% oil, it should be possible to

recover approximately 80% of the oil by phase separation at 30° C. If a portion of the water phase was recycled back through the extractor, a further amount of oil could be recovered. However, it is not possible by this process to separate all of the oil from the impurities and a considerable amount of valuable oil and fatty acids would be mixed with the gossypol and other impurities sent to the evaporator for solvent recovery.

Further tests of phase relationships in systems containing hexane, isopropanol, and water indicated considerable possibility in a miscella recovery method based on liquid-liquid extractions. Preliminary qualitative work has been carried out using an 8 ft. high, 1½ in. diameter glass column packed with ⅜-in. glass Raschig rings.

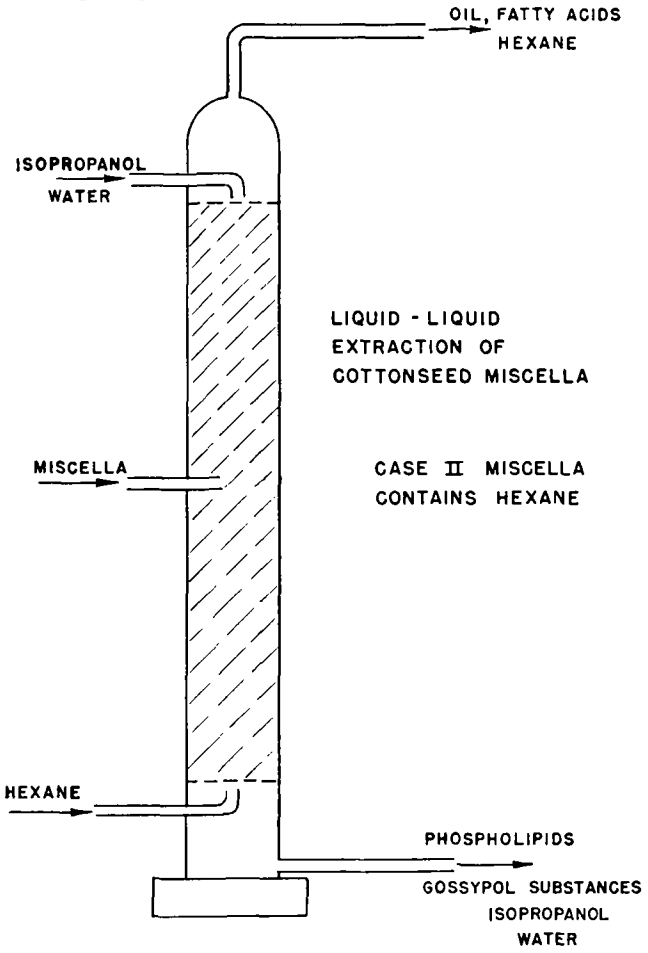


FIG. 7.

The flow diagram, Figure 6, shows the treatment of a hexane-free miscella to completely separate oil from fatty acids, phosphatides, and gossypol. Miscella is fed to the center of the extraction column where it distributes between an oil phase and an isopropanol water phase. Since the oil phase is heavier, it moves downward. A fresh isopropanol-water mixture is fed in the bottom of the column to strip the oil of impurities. In the upper section of the column the water-isopropanol phase is stripped of oil and enriched in impurities by a reflux stream fed back into the top. The reflux stream is obtained by addition of water to the isopropanol water phase to separate the oil, or by evaporation of a portion of the solvent to accomplish the same purpose.

Figure 7 shows the method used for treating a miscella which contained hexane and isopropanol. In this case oil and fatty acids were separated from phospholipids and gossypol substances. Also by this process, the overhead stream from the first column, which contains fatty acids and impurities, may be further separated to obtain a fraction rich in fatty acids.

The miscella (or extract from the first column) is again fed into the center portion of an extraction column. In this column, the oil phase will contain enough hexane so that it is lightest and rises in the column. Fatty acids, as well as oil, are more soluble in the hexane phase and are therefore carried up the column. Isopropanol-water mixture is fed into the top of the column to strip the hexane phase of impurities (gossypol and phospholipids). The isopropanol-water phase passes on down the column and is stripped of oil components by feeding hexane in the bottom.

All product streams are fed to evaporators to recover the solvents except that the alcohol may be separated from the oil stream by water washing. Solvent vapors may be fed into an azeotropic still to separate the hexane, water, and isopropanol. This is possible since hexane forms a ternary constant boiling mixture containing alcohol and water, which stratifies into two layers. Water is removed by a separation of these layers.

Discussion

This work has indicated that there are three possibilities in the use of isopropanol for extraction of cottonseed. These are: (1) The use of low alcohol concentrations, i.e. 91%; (2) the use of high alcohol concentrations, 95-100%; and (3) the use of hexane-isopropanol mixtures. On a basis of oil solubility, 91% isopropanol is approximately a minimum feasible concentration to use. On the other hand, it may be desirable to use higher alcohol concentrations at somewhat lower temperatures to prevent the extraction of considerable quantities of sugars inasmuch as these sugars have no present market value. This object may also be accomplished by using hexane-alcohol mixtures.

Since isopropanol has a high heat of vaporization, the use of isopropanol-hexane mixtures would lower steam costs for solvent recovery, but would result in decreased efficiency of gossypol extraction and an increased fire hazard. One of the advantages of isopropanol is its low fire or explosion hazard when compared to hexane.

The additional quantity of solvents used in the liquid-liquid extraction method of treating the miscella should not be great since the impurities represent only a small portion of the extracted material and the separation factors are favorable. The added cost of recovering these solvents should be more than counterbalanced by the increased value of a fatty acid-free oil, and a fatty acid concentrate.

Summary

Phase equilibrium data for the system; cottonseed oil-isopropanol-water were determined at 30° C. and compared with data for the system; cottonseed oil-ethanol-water. The relative phase distribution of fatty acids and cottonseed oil in mixtures with isopropanol and water was studied under varying conditions of water and fatty acid concentrations. These

tests showed the fatty acids to be highly concentrated in the alcohol-water phase.

Flaked cottonseed meats were extracted in continuous extraction apparatus with 91% isopropanol, 99% isopropanol, and mixtures of commercial hexane and isopropanol. Analytical data on the extractions show that 91% isopropanol is an efficient solvent for extracting active gossypol along with the oil.

Rat and swine feeding tests of the isopropanol extracted meal showed it to be highly superior to hydraulic meal as a source of protein.

A method was developed for treatment of the cottonseed-isopropanol miscella by liquid-liquid extraction to separate purified oil and fatty acid fractions from other materials in the extract.

Acknowledgments

This work was carried out with funds from the Cotton Research Committee of Texas and the Texas Engineering Experiment Station.

Appreciation is expressed to B. R. Holland for assistance in the gossypol determinations.

REFERENCES

1. Vix, H. L. E., Pollard, E. F., Spadaro, J. J., and Gastrock, E. A., Ind. Eng. Chem., *38*, 635-642 (1946).
2. Mozgov, I. E., Veterinariya, *23*, 38-42 (1946); C. A., *40*, 7393 (1946).
3. Lyman, C. M., Holland, B. R., and Hale, F., Ind. Eng. Chem., *35*, 188-190 (1944).
4. Boatner, C. H., Hall, C. M., O'Conner, R. T., Castillon, L. E., and Curet, M. C., J. Am. Oil Chem. Soc., *24*, 97-106 (1947).
5. Olcott, H. S., and Fontaine, T. D., J. Nutr. *22*, 431-437 (1941).
6. May, C. E., A System of Organic Chemistry, 161 (1941).
7. Van Dijeck, W. J. D., U. S. Pat. 2,268,786 (1942).
8. Smith, F. H., Ind. Eng. Chem., An. Ed., *18*, 43-45 (1946).

Soap Content of Some Commercially Refined Oils; Effect of Soap on the Bleachability of the Oils

WALES NEWBY

Opelousas Oil Refinery Cotton Products Company, Inc.
Opelousas, La.

IN the commercial refining of vegetable oils by means of an alkali, such as sodium hydroxide, there is always a small residue of soap left in the oil. Various procedures, as waterwashing and filtering are used to remove these traces of soap, but even after washing and filtering there is usually a detectable trace of mineral matter, presumably largely sodium, left. That the determination of these traces of residual soap is important is well attested by the numerous articles (2, 3, 4, 5) which have appeared describing and discussing analytical methods adapted to their estimation. However, there is very little in the literature regarding the results which are obtained when these analytical methods are applied to commercial oil products.

The report of the A.O.C.S. Soap in Refined Oil Committee for 1936, contained the following statement, "A freshly refined oil will contain from 0.05% to 0.15% of soap depending on the oil and method of neutralization. After bleaching this content will be reduced to below 0.005%." No actual analytical values were shown however, except for those obtained in the cooperative work on selected samples and directed at evolving a satisfactory analytical method. Boekenoogen (3) reported some values for soap in refined cottonseed oil, but his work was concerned largely with methods of analysis and the solubility of sodium soap in cottonseed oil.

Part of the reason for the lack of reported values for soap in commercially refined oils may lie in the somewhat unreliable nature of the analytical methods available (5). Regardless of the reliability of the methods, however, the refinery chemist is often called upon to make determinations of soap in refined oil, and, in the absence of any published values, he may find it difficult to form an opinion as to whether a given result is reasonable or not. It is believed, therefore, that the results reported here will be of some interest.

Samples have been analyzed and results compiled to show the amount of soap remaining in refined cottonseed and soybean oils at various steps in the continuous centrifugal refining process using sodium hydroxide as the neutralizing agent and employing a single stage of waterwashing. At the same time experiments were conducted to determine what effect an excessive amount of soap remaining in a refined oil might have on its bleachability and how effective the bleaching would be in removing the excess soap. The results reported were taken from analyses run in the laboratories of two independent refineries on oils produced in the respective refineries. Since the two sets of results are in agreement, it seems reasonable to assume that they are representative of average commercial oils refined under similar conditions.

Description of Refining Process and Definition of Terms

The process by which the oils were refined has been described in detail by James (6), and it is probable that most readers will be familiar with the terms which will be used to identify the samples analyzed. A brief description of the process, however, with particular references to the points at which sampling was done, will be given. Crude oil, upon entering the refinery, is mixed with a definite volume of sodium hydroxide solution in closed mechanical mixers. The emulsion thus formed is led into a heater where it is heated and the emulsion broken. At this point most of the sodium hydroxide has combined with the free fatty acids and other acidic impurities present to form flocs of hydrated soap which occlude other insoluble impurities. The neutralized oil containing the precipitated soap and impurities is then passed through a set of continuous centrifuges, which separate more or less completely the clear oil from the suspended soap and impurities. These centrifuges which separate the bulk of the soap from the refined