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A Study of Extraction Rates for Cottonseed and Soybean Flakes Using n-Hexane and Various Alcohol-Hexane Mixtures

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IT has long been recognized that alcohols and hydrocarbons are effective solvents for extracting oils from oil-bearing materials; however there appears to be little, if any, work reported on the effects of mixtures of these materials and their effects on extraction rates. The data contained herein are a study of extraction rates of vegetable oils with Phillips Commercial *n*-Hexane and the effects on the extraction rates of the addition of small amounts of various alcohols to the *n*-hexane.

The purpose of these tests was to determine the effects of adding to commercial *n*-hexane those materials which would azeotrope with *n*-hexane to determine if the extractions of vegetable oils could be accelerated.

Both cottonseeds and soybeans were employed in these tests. Although the general characteristics of extraction were similar, differences were discernible between the data for each material.

All studies of extraction rates were batch-wise extractions and cannot be interpreted directly as applicable to countercurrent extraction work. However the basic principles of extraction and the basic effects of the various additives should show a trend that could be expected when oil-bearing materials are extracted by the various solvents and solvent mixtures. Some countercurrent extractions were made in a laboratory countercurrent extractor to determine the quality of the oil produced by extracting with a methanol-hexane mixture.

Experimental

A. *Equipment and Materials.* Two sets of extraction equipment were employed in these studies. The rate studies were conducted in a batch extractor while other extractions were made in the laboratory countercurrent extractor. The latter extractions were made to provide sufficient quantities of oil for determinations of oil quality.

Figure 7 is a schematic drawing which depicts the apparatus used in the batch-wise extraction rate studies. The equipment consisted essentially of an extraction thimble, heating jacket for the thimble, a constant volume flow pump, solvent storage flask, and preheaters. The thimble was made from a section of glass tubing 22 mm. (I.D.) in diameter and 100 mm. in length. The sealed end of the thimble was perforated with 16 small holes to allow the miscella to drain from the thimble but to force all of the solvent to percolate through the whole length of the thimble. The heating jacket for the thimble consisted of an electrically heated glass shell which also held the thimble in the extraction position. A stainless steel diaphragm pump was set to pump the preheated solvent from the storage flask to the extraction thimble at a constant rate. All of the solvent transfer lines were electrically heated and insulated.

The laboratory countercurrent extractor is the same as the one employed in other extraction work and is described in detail in a previous publication (1).

Soybean flakes used in these studies were commercially flaked beans obtained from Cargill Inc., Minneapolis, Minnesota. Commercially dehulled and delinted cottonseeds were obtained from Helena Cotton Oil Company, Helena, Arkansas, and Delta Products Company, Wilson, Arkansas. The cottonseeds were flaked in the laboratory and were of an average flake thickness of 0.01 inch. Low moisture contents were desired and therefore the moisture and volatile contents (Ba 2-38) were maintained between 6 and 8%.

The solvents employed and compared in these studies were as follows:

Control solvent:
  Phillips Commercial *n*-Hexane

Test solvents, mixtures:
  5% Methyl alcohol in comm. *n*-hexane
  5% Ethyl alcohol in comm. *n*-hexane
  5% Isopropyl alcohol in comm. *n*-hexane
  5% Allyl alcohol in comm. *n*-hexane

All percentages were measured by volume at room temperature.

B. *Procedure.* The data from two procedures are considered in these studies. All of the extraction rate data were obtained from batch-wise extractions while the data relating to the quality of the oils were obtained from extracting the seeds in the laboratory countercurrent extractor.

In the batch-wise extraction rate studies an 8-g. sample was weighed to the nearest 0.0005 g. A piece of glass wool was placed in the bottom of the extraction thimble to prevent the passage of "fines" with the miscella. The flakes to be extracted were placed in the thimble on top of the glass wool mat and tamped firmly to reduce channeling. The flakes were covered with a small layer of glass wool to assist in distribution of the solvent and to prevent flake flotation. After a thermocouple had been inserted into the center of the flake bed, the thimble was placed in the thimble heating jacket and secured in place just below the solvent inlet and condenser. While the solvent storage flask and solvent transfer lines were being heated, the flakes were also brought to the desired extraction temperature. When the proper temperature was reached, the extraction process was started and the time was measured from the first flow of solvent into the thimble. The solvent rate was maintained at 10 ± 1 milliliters per minute. Exact temperature control was never attained. The solvents were kept at temperatures below the boiling points of the azeotropes while the flake bed was maintained between 120-130F. The miscella was collected in tared beakers for designated time intervals. The excess solvent from the collected miscellas was removed by heating the beaker on a hot plate while extraction proceeded. The remaining solvent was removed from the oil in a vacuum oven at 170F.(77C.) where the beakers containing the oil samples were brought to a constant weight.

Samples were taken periodically throughout the extraction period. The intervals of sampling in these studies were: 2 min., 5 min., 15 min., 30 min., 50 min., 70 min., 100 min., 130 min., and 160 min. Each sample consisted of the total miscella which was collected during each time interval. After a total of 160 minutes extraction time had elapsed, the solvent flow was stopped, and the flakes were removed from the thimble and ground with mortar and pestle. The ground flakes were then placed on No. 2 Whatman filter paper, rolled into a thimble, and placed in a Butt extractor where they were exhaustively extracted with the same solvent which had been used in the original extraction. After exhaustive extraction (five hours at the boiling point of the solvent) in the Butt extractor, the miscella and flask were removed; the solvent was evaporated, and the flask was brought to a constant weight in a vacuum oven to determine the amount of residual oil. The relative rates at which oil was removed from the flakes were determined from the data for the increments of oil and the percentage of total oil extracted.

The extraction procedure employed with the countercurrent extractor was essentially the same as that described in a previous article (1). The following analyses recommended by the American Oil Chemists' Society were employed: Moisture and Volatile Matter in the Flakes and Meal (Ba 2-38); and Free Fatty Acids (Ca 5-40). In addition, Refining Loss (Ca 9a-41) was modified to use only a 100-g. sample and to separate the oil from the soapstock by centrifuging the mixture.

C. *Data Correlation.* The data obtained from the batch extractions were used to make various calculations which applied directly to extraction rates. However the data presented in the accompanying figures (Figure 1 through Figure 6) were correlated by four methods and curves plotted from the averaged results from duplicate runs.

The four methods of data correlation were made to provide a comparison of solvents from several different aspects since a true evaluation of the solvents was not possible from a single correlation. The correlations employed and presented in graphical form are: 1) the percentage of oil recovered, *versus* time in minutes; 2) the percentage of residual oil, *versus* time in minutes; 3) the percentage of extractable oil remaining in the flakes, *versus* time in minutes; and 4) the rate of extraction (change in the percentage of oil removed per unit change in time), *versus* time in minutes. All calculations for the flakes and meals were normalized to a moisture-free basis.

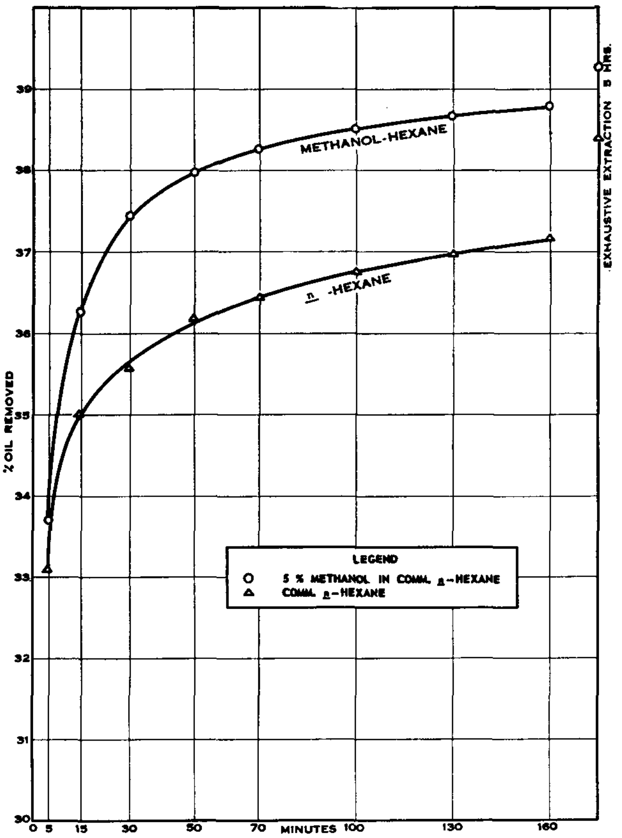

FIG. 1. Group 1, cottonseeds. Correlation 1, per cent oil removed *vs.* time.

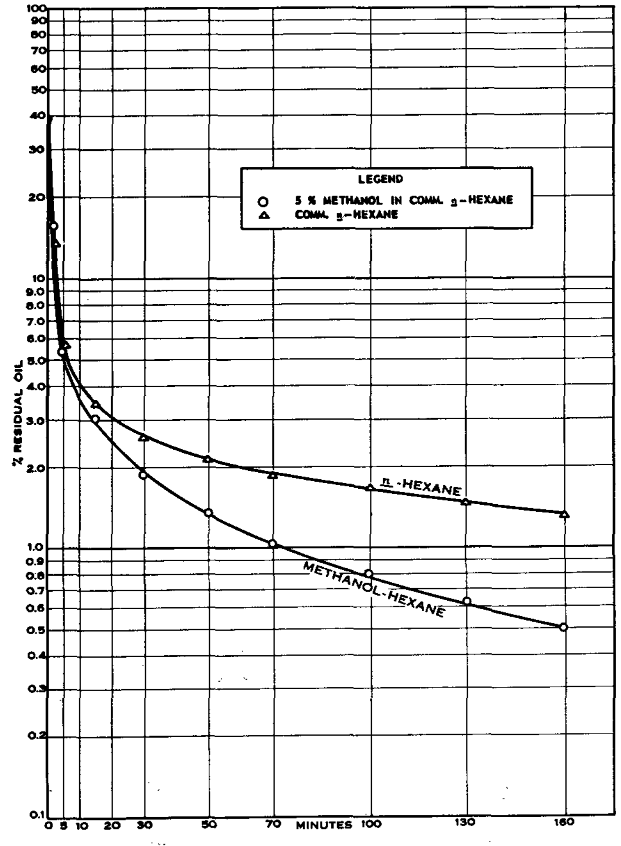

FIG. 2. Group 1, cottonseeds. Correlation 2, per cent residual oil *vs.* time.

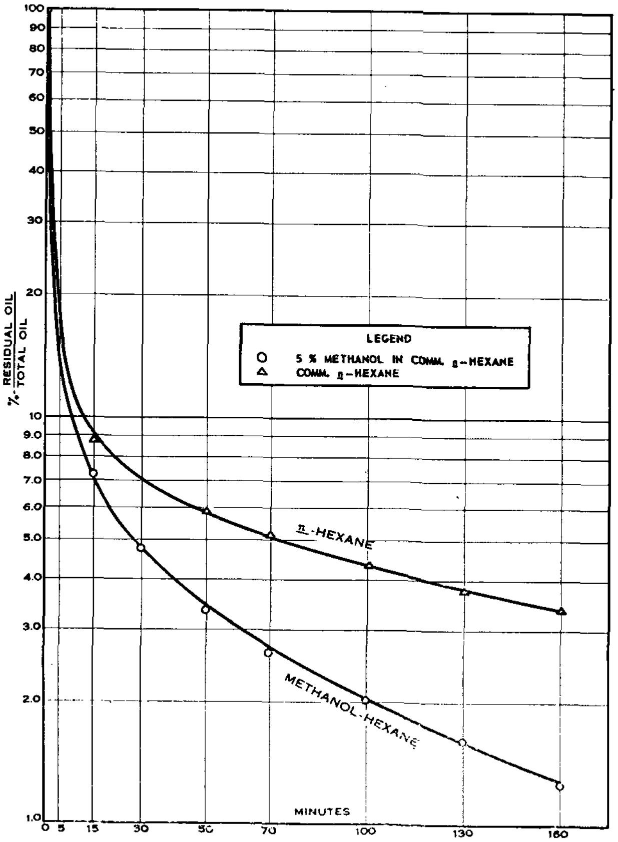

Fig. 3. Group 1, cottonseeds. Correlation 3, per cent residual oil/total oil *vs.* time.

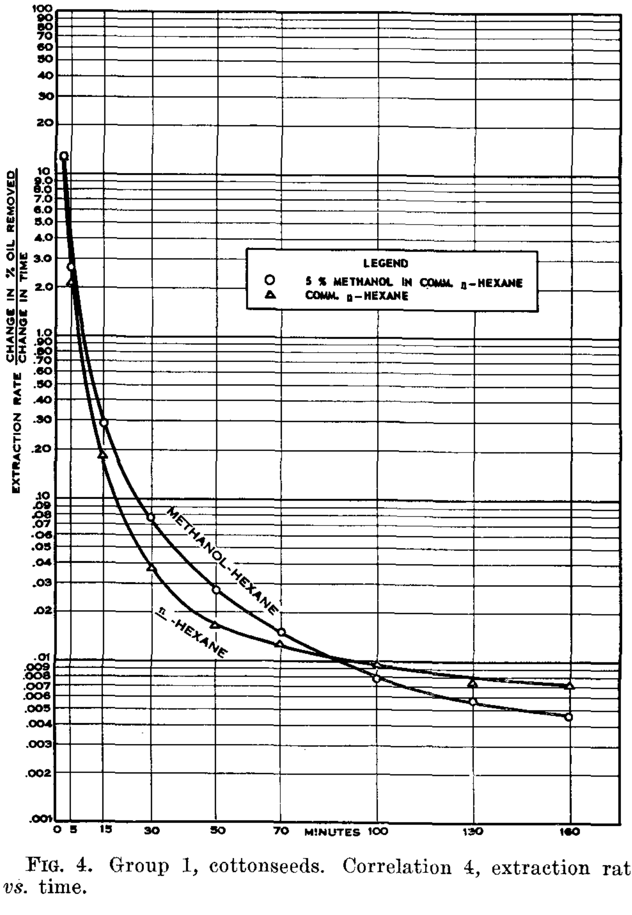

Fig. 4. Group 1, cottonseeds. Correlation 4, extraction rate *vs.* time.

Correlation 1) is presented in Figures 1, 5, and 6. The curves in each one of these figures represent the averaged data from one or more runs on separate materials. Figure 1 represents the percentage of oil removed from bone-dry cottonseed flakes plotted, *versus* time in minutes, for 5 *n*-hexane extractions and compared with data from 2 extractions with a methanol-hexane mixture. Here the methanol-hexane mixture shows a definite superiority in having removed more oil at any given time and apparently is removing more oil at a faster rate than the *n*-hexane.

For a similar group of cottonseed flakes Figure 5 represents the averaged data for extractions by the following solvents: 3 runs with *n*-hexane, 2 runs with methanol-hexane mixture, and 1 run each with mixtures of ethanol-hexane, isopropanol-hexane, and allyl alcohol-hexane. The superiority of the methanol-hexane mixture over *n*-hexane is also apparent in this series of runs. At the same time it appears to be superior to the other alcohol mixtures considered. Each of the mixtures has removed more oil at any given time during the extraction than was removed by *n*-hexane. The total oil removed at the end of the exhaustive extraction is also included in these figures and is, in every case, higher than that extracted by *n*-hexane. The percentage of oil removed by the mixtures as compared with *n*-hexane appear in the following order of decreasing amounts: methyl alcohol, ethyl alcohol, isopropyl alcohol, and allyl alcohol.

Data from extractions of soybean flakes by *n*-hexane and various alcohol-hexane mixtures are presented in Figure 6. These data are averages from 2 extractions by *n*-hexane, 2 extractions by a methanol-hexane mixture, 2 extractions by an allyl alcohol-hexane mixture, and 1 extraction by an isopropyl alcohol-hexane mixture. The same general trend can be observed from the soybean extractions as was noted with cottonseeds. The alcohol-hexane mixtures appear to have removed more oil at any given time than the *n*-hexane, but the methanol-hexane mixture still shows some superiority over the others. The percentage of oil removed by the mixtures as compared with *n*-hexane appears in the following order of decreasing amounts: methanol-hexane, allyl alcohol-hexane, isopropanol-hexane.

The data as presented in this correlation are not only significant in showing the amount of oil removed at any given time during the extraction but are also significant in giving a comparison of the rates of extraction. The slope of each curve is indicative of the extraction rate. Although the alcohol-hexane mixtures all tend to remove more oil for a given time, the methanol-hexane mixture is outstanding in every case, by removing more oil at a faster rate.

Correlation 2), which shows the percentage of residual oil in the flakes at any given time during the extraction, is presented in Figure 2. Figure 2 presents in graphical form the averaged data for one group of cottonseed flakes and compares *n*-hexane with methanol-hexane mixtures. At any given time after the first 5 minutes of extraction the methanol-hexane mixture shows a lower residual oil content than that of *n*-hexane. This type of correlation is presented since commercial plant analyses are based on residual oil contents of the extracted flakes rather than the amounts of oil removed.

The data in correlation 2) are presented on semi-log paper in order to include all of the extraction

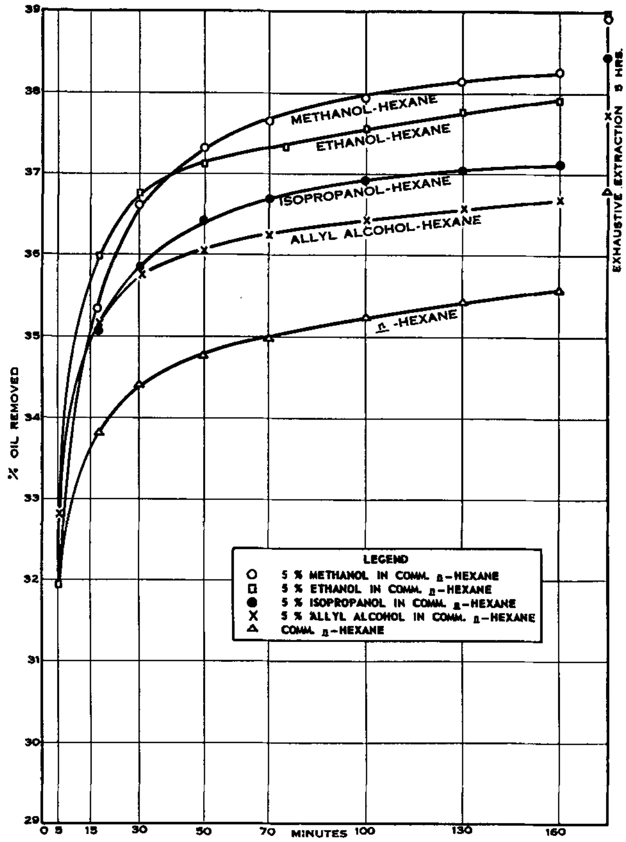

FIG. 5. Group 2, cottonseeds. Correlation 1, per cent oil removed *vs.* time.

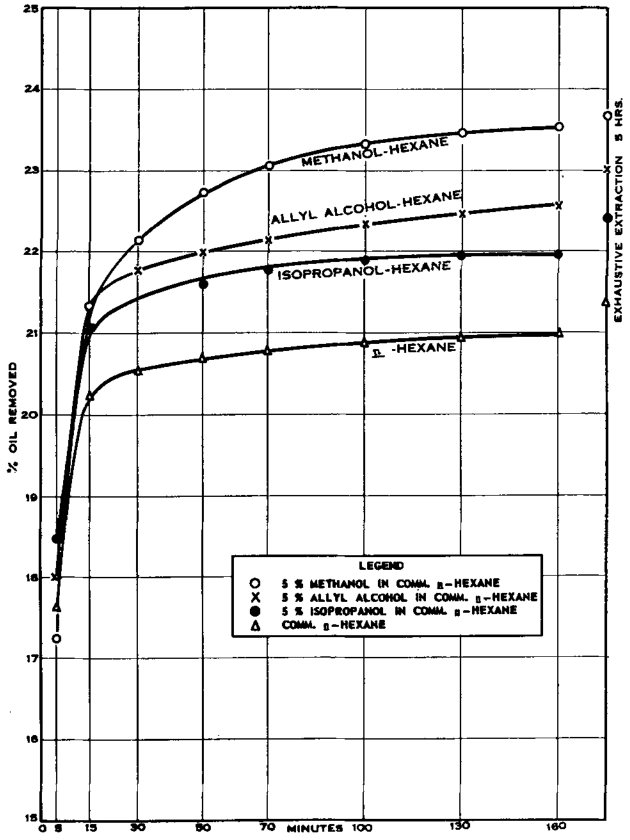

FIG. 6. Group 3, soybeans. Correlation 1, per cent oil removed *vs.* time.

data on a manageable graph. The slopes of the curves as plotted on semi-log graphs do not show the extraction rate but represent a function of the extraction rate. Since the curves are for comparative purposes only, indications of extraction rates may be understood without plotting the true extraction rate curve.

Correlation 3) is an attempt to correlate the residual oil data with compensation of the variations in the total oil yields. In Figure 3 the residual oil divided by the total oil yield is plotted, *versus* extraction time in minutes. This presents a somewhat clearer picture of the residual oil data. Here the extractions for one group of cottonseeds are compared for the methanol-hexane mixture and for *n*-hexane. The methanol-hexane mixture shows a lower amount of residual oil at any given time during the extraction after the initial stages of extraction than does the *n*-hexane. Here also the slopes of the curves do not give true extraction rates but may be used for comparative purposes.

Figure 4 depicts correlation 4) in which extraction rates are plotted, *versus* time. This correlation is derived by plotting the changes in percentage of oil removed, divided by changes of time in minutes, *versus* time in minutes, and are therefore directly representative of changes in extraction rates. Any point on the curve represents a particular rate at a particular time during extraction; therefore if the slopes of the curves were considered, they would be a function of the rate of change in extraction rates, or acceleration.

From about 5 minutes extraction time to approximately 90 minutes extraction time, Figure 4 indicates greater changes in extraction rates for the methanol-hexane mixture than for *n*-hexane extractions. At the end of 90 minutes extraction time the methanol-hexane mixture shows smaller changes in rates of extraction due to the lower residual oil content of the flakes. The differences in rates are more apparent after the initial stages of extraction and remain so until the latter stages of extraction known as the "period of difficult solubility."

A comparison of the quality of cottonseed oil recovered by countercurrent extraction of cottonseed flakes by *n*-hexane and a 5-95% methanol-hexane mixture is presented in Table I. Both the free fatty acid contents and refining losses indicate little or no variation in the quality of the oil extracted by either solvent.

In the last two comparative countercurrent extractions it will be noticed that the refining losses are greater than in the first two extractions. This, of course, is due to the increased fatty acid content caused by aging of the flakes. There is an indication that on poorer flakes (damaged or old seeds) the methanol-hexane mixture might show even a superior selectivity than on flakes of lower free fatty acid content.

TABLE I

Analyses of Cottonseed Oil Extracted Countercurrently by *n*-Hexane and a 5% Methanol-95% Hexane Mixture

Solvent	Flake rate	Solvent rate	Oil content		FFA	Refining loss
			Flakes	Resid. oil		
	g./min.	*g./min.*	%	%	%	%
MeOH-C_6	5.17	13.77	34.0	1.6	2.8	9.8
n-C_6	5.25	14.28	34.4	2.1	2.8	9.7
MeOH-C_6	5.46	14.50	33.6	2.2	3.2	10.9
n-C_6	5.15	12.96	35.5	2.9	3.8	12.0

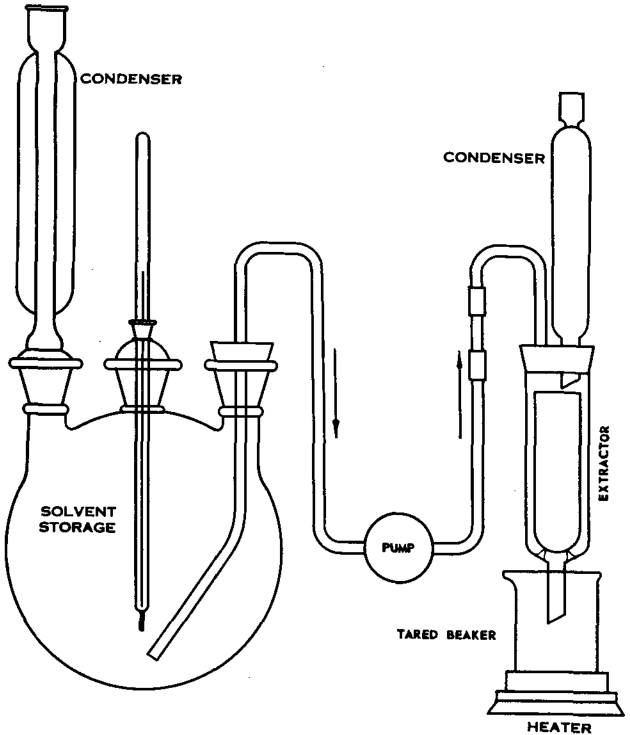

FIG. 7. Batch extractor.

The residual oil contents of meal from the methanol-hexane extractions were lower than those from *n*-hexane extractions. The qualities of the oils extracted by the mixture were comparable to those extracted by *n*-hexane.

Discussion

The percolation of solvent through a fixed bed of oleaginous flakes employed to provide extraction rate data in these tests had previously been employed by Wingard (2) to obtain preliminary data for the design of vegetable oil extraction equipment. The tests of Wingard and those previously conducted by King (3) indicate that during the initial phases of extraction the oil is removed very rapidly, but as the extraction proceeds, the extraction rate becomes exceedingly slow. Karnofsky (4) has proposed that the mechanism of extraction appears to be a combination of diffusion and the solution of a slowly soluble extractable material. The latter theory assumes that the oil acts as a slowly dissolving material. Certain constituents of the oil are removed "in quantity" only during the final stages of extraction, indicating that these materials may act according to this theory. Multiple stage extractions of soybean flakes, previously conducted in this laboratory, indicate that quality of the crude oil becomes progressively poorer in the final stages of extraction. It has been pointed out that certain of the slow dissolving constituents in the extractables may retard the solution of oil. Since this type of mechanism apparently becomes predominant during the final phase of extraction, it is the determining factor in the design of oil extraction equipment. Wingard also determined that considerable variation in extraction rate could be obtained by varying the solvent employed. Variations in extraction rates were also noted when beans or seeds of a specific type, such as soybeans grown in different fields, were compared. In general, the observations of King and Wingard have been confirmed by the data reported herein. Correlation of this type of extraction data with countercurrent extraction data has not been found in the literature.

The material being extracted should first be defined before other aspects of extraction are considered. If the material removed were a single compound or even a group of related compounds, such as a homologous series, definition of extractables would be relatively simple. Unfortunately in natural products, such as soybeans and cottonseeds, this is not the case. In addition to the fatty acid glycerides which show considerable diversification in the individual acids which are attached to the various glyceride molecules, the extracted crude oils contain a variety of free fatty acids, phosphatides, carotene, tocopherols, sterols, hydrocarbons, color bodies, and other extraneous materials. The proportion of non-glyceride components of the crude oil is dependent upon the oil-bearing material being extracted, the selectivity of the solvent, the temperature of extraction, the moisture content of the flakes during extraction, and the heat treatment history of the seeds prior to extraction.

A standard analytical method has been adopted by the American Oil Chemists' Society, using a Butt extractor and specifying the drying and grinding pretreatment of the seeds or meal, the solvent (a petroleum ether), extraction time, and reflux rate. This procedure is universally employed in extraction plants and is the legal standard. However for extraction studies for research purposes it appeared desirable to define total extractables (oil) as the total amount of material which could be removed by the solvent under investigation. Calculation of the extraction data could then be made independent of variable amounts of material which could be removed by a given solvent. Since practically the solvent must be evaluated by the A.O.C.S. methods, meal analyses from the countercurrent extractions were subjected to standard analyses with the specified petroleum ether as the extraction solvent.

The total material which could be extracted by any of the alcohol-hexane mixtures exceeded that which could be removed by *n*-hexane. It would be expected that the additional material removed by the alcohol-hexane solvents would be predominantly phosphatidic since alcohols are known to be much better solvents for this type of material than saturated hydrocarbons. Also even after exhaustive extraction with hydrocarbons most meals contain considerable phosphatides. However the refining losses of oils extracted by either the *n*-hexane or the methanol-hexane mixture in the countercurrent extractor were nearly identical when normalized to a common free fatty acid content. This indicates that additional experimentation would be necessary to establish the identity of the extract from the alcohol-hexane mixture.

At a given time after the first few minutes of extraction and before exhaustive extraction, more extractable material is removed from either soybean or cottonseed flakes by alcohol-hexane mixtures than by *n*-hexane. Some discrepancies occur during the first few minutes of extraction when the oil is being removed very rapidly, and factors such as variations in the porosity and permeability of the flake bed greatly affect the apparent rate of extraction. However as the extraction proceeds, the effect of these variations, within the limits encountered in these tests, becomes negligible. The residual oil in partially extracted flakes, after being subjected to extraction for a given time, was greater with some of the alcohol-hexane mixtures than with *n*-hexane. This of course is due to the ability of the alcohol to remove more total material. The methanol-hexane solvent consistently left lower oil residues in either soybean or cottonseed flakes than did *n*-hexane at similar residence times.

Although these preliminary studies indicate a usefulness for this type of solvent extraction, the true merit of an alcohol-hexane mixture could only be established by continued research including plant-scale operations.

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The Relationship Between the Greying of Textiles and the Frictional Electricity Generated in Organic Solvent Systems

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THE importance of frictional electric phenomena for dry cleaning operations is well known (1), and many attempts have been made to lessen the fire hazard which they constitute (2), as well as to counteract so-called lint transfer and insufficient soil removal or whiteness retention (3).

Approximate figures only are given in the literature for the observed voltages and amperages of frictional electricity, which may be due to the fact that such data are a function of the relative size of the equipment and agitation, which could be standardized and controlled though. It may also be due to the fact that the experimentally found voltages and amperages show little reproducibility when repeated under seemingly identical conditions. In our experience this is due to the large effect which vibrations and minute eccentricities of moving parts have on the agitation of fluids, especially when combined with the influence of mechanical handling, temperature, and humidity on the "matting" or stress of the textiles which are part of the equipment. In our experimentations a given set of voltage readings duplicated with a precision of better than ± 30%. Certain other facts duplicated with such precision that we are encouraged to make the following report.

Equipment and Method

Electrical Measurements (See Figure 1). A solvent "B" is placed into a metal cell "C" which acts as electrode and shield. Mechanical agitation is produced by the shaft "D," mounted in styrene and acting as the "hot" electrode. The shaft ends at "E" in a paddle, roller or frame, made of, or covered by any desired material. The electric current produced in this cell is observed in the amplifier "A" as an equilibrium between the internal circuit of the cell and the external circuit of the amplifier (Range: 7.5 milliamp to 1×10^{-14} amp.) (4).

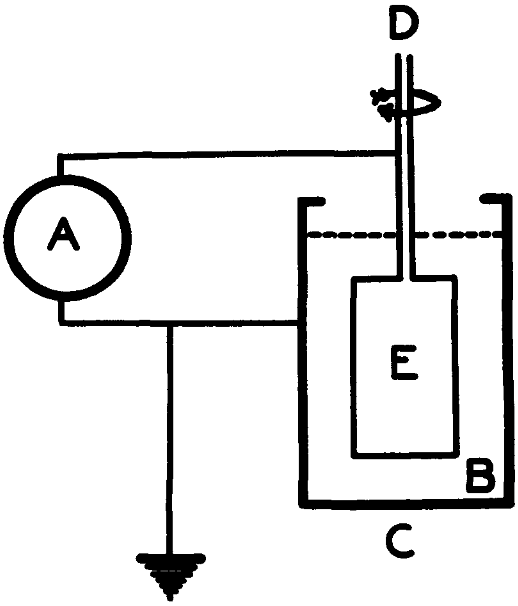

FIG. 1

We have experimented with a variety of sizes and shapes of the cell "C" and the rotor "E." However the experiments were carried out in a cylindrical cell, 3 in. high and 2 in. diameter, with a cylindrical rotor (2 in. high and $\frac{7}{8}$ in. diameter) made of stainless steel. The middle $1\frac{3}{4}$ in. of the rollers height of electric furnace colloidal graphite in mineral oil. were covered by a sleeve of medium weight wool flannel. The cell was filled with 100 ml. fluid and the roller rotated with 300 r.p.m.

Greying Tests. 250-ml. glass bottles with aluminum lined screw caps were clamped upright just above a horizontal shaft which rotated at 42 r.p.m. 100 ml. fluid, 30 stainless steel balls ($\frac{5}{32}$ inch O.D.), 0.0100 ml. oil-dag (an about 10 weight percentage suspension of electric furnace colloidal graphite in mineral oil. The average particle size of carbon is approximately 1 micron), 0.30 g. stearic acid, and one $3\frac{1}{2}$ by $3\frac{1}{2}$ in. sample of white wool-rayon gabardine were tumbled for 10 minutes.

The amount of greying can be determined either by comparing the light reflectivity of the textile sample before and after the test, or by measuring the transmittancy of the fluid (5). Before the test the