· Technical

Application of Ternary Equilibrium Data to the Production of Fish Protein Concentrate

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ABSTRACT

Standard chemical engineering techniques were applied to ternary equilibria data obtained from laboratory studies for the systems water-isopropyl alcohol-menhaden oil and water-ethanol-menhaden oil to obtain information for development and operation of a fish protein concentrate process. Theoretical minimum solvent ratios, the required number of theoretical stages, stage efficiency, effect of excess water in the solvent and the effect of temperature of extraction are reported. A comparison of the solvent, isopropyl alcohol (IPA) and ethanol, at an extraction temperature of 70 C, leaves no doubt that IPA is a superior solvent for the system studied.

INTRODUCTION

The simultaneous extraction of oil and water from fish and fish products to produce fish protein concentrate (FPC) has been reported in the literature for several years (1). Several solvent extraction systems have been reported, and three of the better known processes use isopropyl alcohol (IPA) (2), ethanol (3) or ethylene dichloride (4) as solvents. The solvent extraction of fish and fish products is generally carried out at or near the azeotropic boiling temperature of the solvent and water. However this relatively high extraction temperature tends to denature the protein and thereby destroys many of the functional properties possessed by the original raw material. The ethylene dichloride extraction process must be carried out at the azeotropic boiling temperature of ethylene dichloride and water (4), but ethanol and IPA extractions can be carried out at a lower temperature.

The work presented in this paper was performed in an effort to apply ternary equilibria data to the solvent extraction of raw menhaden, in order to determine the theoretical minimum solvent ratios and the number of ideal extraction stages required to produce a protein concentrate with less than 0.5% residual lipids as required by Food and Drug Administration regulations (5). Similar work has been reported for the IPA extraction of chicken meat (6). The effect of a few operating variables is also reported. Menhaden *(Brevoortia tyrannus)* were chosen for this study, because they are caught in abundant quantities and are one of many species suitable for the production of FPC.

EXPERIMENTAL PROCEDURES

To determine minimum solvent ratios required for the extraction of menhaden, ternary equilibrium data for the systems water-IPA-menhaden oil and water-ethanol-menhaden oil were used. These data have been previously reported and described in detail (7).

To calculate the number of extraction stages needed to produce a FPC, additional data were required to obtain an underflow line. The underflow line for a solid-liquid extraction is a plot of the mass ratio of the solid to the retained solution as a function of the concentration of the solution. Data for the underflow line must be determined experimentally under conditions of the extraction. To obtain the necessary data for its construction, several laboratory extractions were carried out at controlled temperatures using either IPA or ethanol as the solvent. Known quantities of solvent were added to 400 g raw, ground menhaden in a fully baffled mixing vessel and agitated. Care was taken to insure that 100% mixing occurred throughout by using the applicable geometric parameter ratios. The mixing process was carried out for 15 min, determined to be more than adequate time to insure the attainment of equilibrium. After the extraction was completed, the liquid was separated from the solids by means of a basket-type centrifuge. Samples of both the liquid and the solid were taken from each extraction and analyzed for per cent volatiles, fat (8) and water (9).

RESULTS

Calculation of Minimum Solvent Ratios

One of the basic requirements for a solid-liquid extraction process is that there must be enough solvent present to dissolve the solute to be extracted. This information can be obtained from ternary equilibrium studies. The ternary equilibrium data previously reported (7), together with additional data obtained from laboratory studies have been plotted in Figures 1-4, using the coordinates x and y where x = the weight fraction of water in solution and y = the weight fraction of oil in solution.

If the raw fish to be extracted contained W lb. of water and F lb. of oil, the minimum amount of solvent S which will remove all the oil and all the water from the raw fish can be calculated from a material balance on the overall extraction process: input + generation = output + accumulation.

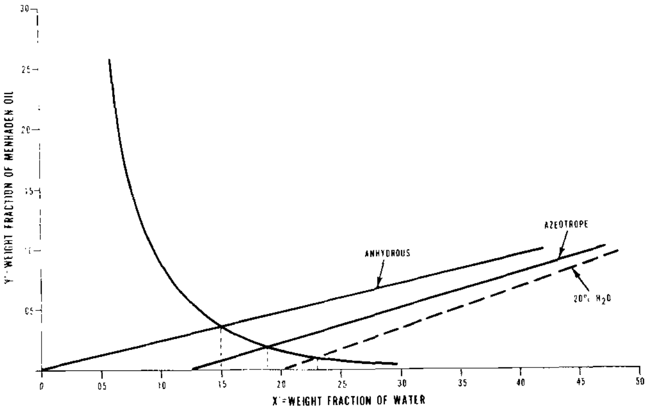

FIG. 1. Water-isopropyl alcohol-menhaden oil equilibrium curve at 50 C.

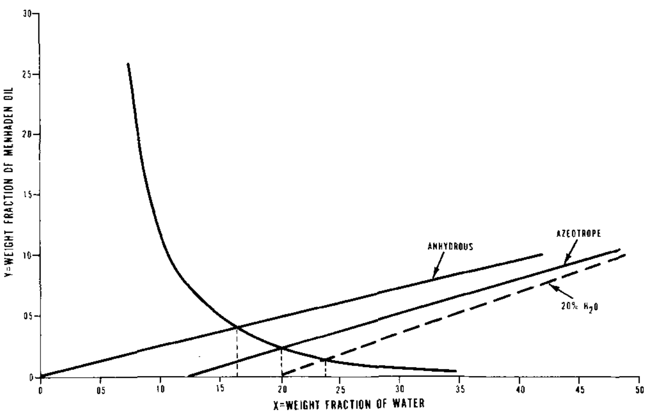

FIG. 2. Water-isopropyl alcohol-menhaden oil equilibrium curve at 60 C.

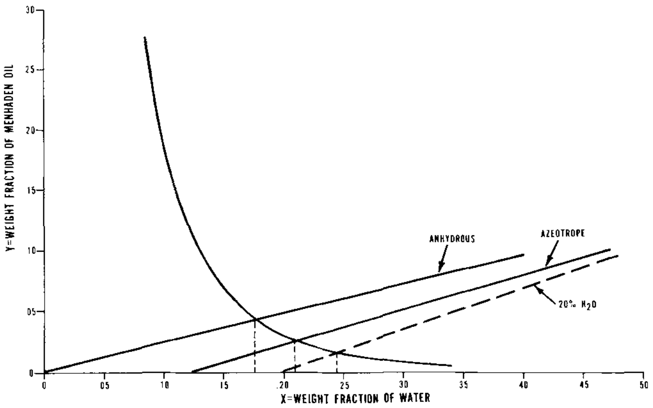

FIG. 3. Water-isopropyl alcohol-menhaden oil equilibrium curve at 70 C.

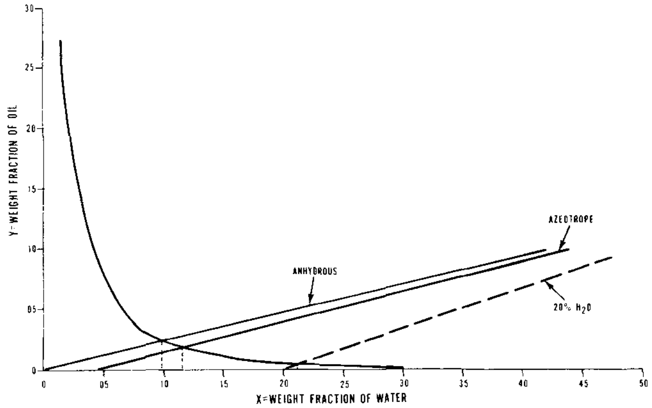

FIG. 4. Water-ethanol-menhaden oil equilibrium curve at 70 C.

Since there is no chemical reaction, the generation term is zero. If we make the simplifying assumption that all the solvent is removed from the fish after extraction, then the accumulation term is also zero, and the solution left after extraction will contain W lb. of water and F lb. of fat. Let Z be the weight fraction of water in the fresh solvent, and, assuming that none of the protein is dissolved in the solvent, we define x and y as follows: x = lb. of water in solution/lb. of solution remaining after extraction and y = lb. of oil in solution/lb. of solution remaining after extraction. Symbolically this can be written as $x = (W+ZS)/(W+F+S)$ and $y = F/(W+F+S)$. Solving these equations for S we get $S = (W-x[W+F])/(x-Z)$ and $S = (F-y[W+F])/y$. Solving for y in terms of x we get: $y = F/(W-Z[W+F])x - (FZ)/(W-Z[W+F])$.

This equation is a linear relationship of the form $Y = AX + B$ and any mixture of solvent and solute should follow this relationship, if the simplifying assumptions stated above hold true. This is the equation of the operating line, and the minimum amount of solvent required for extraction would be that amount of solvent in which y is the weight fraction of oil in a saturated solution.

The above relationship is quite general, and to take into consideration the fact that the residual oil content of the fish need be reduced only to 0.5% (5) and the residual water content may be reduced to ca. 12.5% with azeotropic IPA, we can redefine the terms in the previous equations as follows: Let $F' = F - 0.005R$ and $W' = W - 0.125R$, where R is the residual solids remaining after extraction. The above equation can be rewritten as: $S = (W' - x[W'+F'])/(x-Z)$ and $S = (F' - y[W' + F'])/y$ and consequently $y = F'/(W'- Z[W' + F'])x - (F'Z)/(W'- Z[W' + F'])$.

To calculate the minimum solvent ratio for the extraction with azeotropic IPA of 100 lb. menhaden having an average oil content of 15.11% and an average water content of 63.82%, we can use the third equation above to determine the operating line and either the first or the second equation to determine the minimum solvent ratio. The average oil and water content of raw menhaden used in the above illustration is an average value for Atlantic Coast menhaden obtained from unpublished data gathered over a 2 year period. Thus for the above data we have: $R = 21.07$; $F' = 15.00$; and $W' = 61.19$.

If the fresh solvent used is azeotropic IPA, then $Z = 0.123$ and the equation for the operating line becomes: $y = 0.289\ x - 0.0356$.

This operating line is plotted in Figures 1-4, and its intersection with the equilibrium curves gives the values of x (or y) for the minimum amount of solvent S. Thus, for extraction of raw menhaden at 60 C with azeotropic IPA, we obtain from Figure 2 the value of $x = 0.202$, and by substituting this value into the first equation we obtain S = 580 lb. solvent. The minimum solvent ratio for IPA at 60 C is 5.8:1. Other minimum solvent ratios are listed in Table I.

To determine the effect of excess water content in the entering solvent, a water content of 20% by weight was assumed for the fresh solvent. The new equation for the operating line becomes: $y = 0.336\ x - 0.0673$.

TABLE I

Effect of Solvent, Temperature and Water Content of the Fresh Solvent on the Minimum Solvent-Solid Ratio Required to Extract Menhaden

		Minimum solvent ratio		
Solvent	Temperature, C	Anhydrous solvent	Azeotropic solvent	20% H_2O in fresh solvent
Isopropyl alcohol	50	3.4:1	7.1:1	15.2:1
Isopropyl alcohol	60	3.0:1	5.8:1	11.0:1
Isopropyl alcohol	70	2.8:1	5.3:1	9.6:1
Ethanol	70	5.7:1	7.5:1	36.4:1

TABLE II

Underflow Curve for Azeotropic Isopropyl Alcohol and Menhaden Fish at 60 C

X lb. oil/lb. oil + IPA	Y lb. solid/lb. oil + IPA
0.346	1.292
0.282	1.345
0.277	1.400
0.227	1.510
0.113	1.855
0.085	1.908
0.072	1.955
0.050	2.016
0.0302	2.042
0.0160	2.051
0.0023	2.0573

This new operating line is shown in Figures 1-4 as a dashed line, and the minimum solvent ratio for extraction at 60 C with IPA under these new conditions becomes 11:1. The effect of this operating variable at other temperatures and with ethanol is also reported in Table I. A similar analysis was carried out for anhydrous solvent, and those results are also presented in Table I.

Determination of the Underflow Curve

The underflow curve was constructed from the data obtained. These data are presented in Table II, and the underflow curve is plotted in Figure 5.

Determination of Overflow Curve and Tie Lines

Due to the fact that the solid is assumed to be insoluble in the solvent, all points representing overflow streams lie on the axis of the abscissa, i.e., where $Y' = O$ in Figure 5 and where Y' is defined as the ratio of solid to solvent plus solute.

If sufficient solvent is present to dissolve all the solute in the entering solid and if there is no adsorption of solute by the solid, equilibrium is attained in a solid-liquid extraction when the composition of the liquid retained by the solid leaving any stage is the same as that of the liquid overflow from the same stage. Therefore all tie lines are vertical when these conditions are met.

Number of Equilibrium Stages

A modification of the Ponchon-Savarit graphic method is described in detail by McCabe and Smith (10) and may be used for solid-liquid extraction calculations when the underflow and overflow vary from stage to stage. This condition occurs when lipids are extracted from a solid fish protein, and consequently the material balance involves only the solute, the solvent and the inert solids.

The conditions that must be met in order to apply this technique are: (a) There must be enough solvent present to dissolve all of the solute; and (b) The contact time between solid and solute must be sufficient to attain equilibrium.

a) *Material balance:* The insert in Figure 5 shows an overall material balance for a solid-liquid extraction process and consists of four streams, namely: the inlet solvent V_b, the outlet solution V_a, the inlet feed L_a and the outlet exhausted solids L_b. An overall material balance can therefore be represented by the equations: $V_b + L_a = J = V_a + L_b$. The J point is described in detail by McCabe and Smith (10).

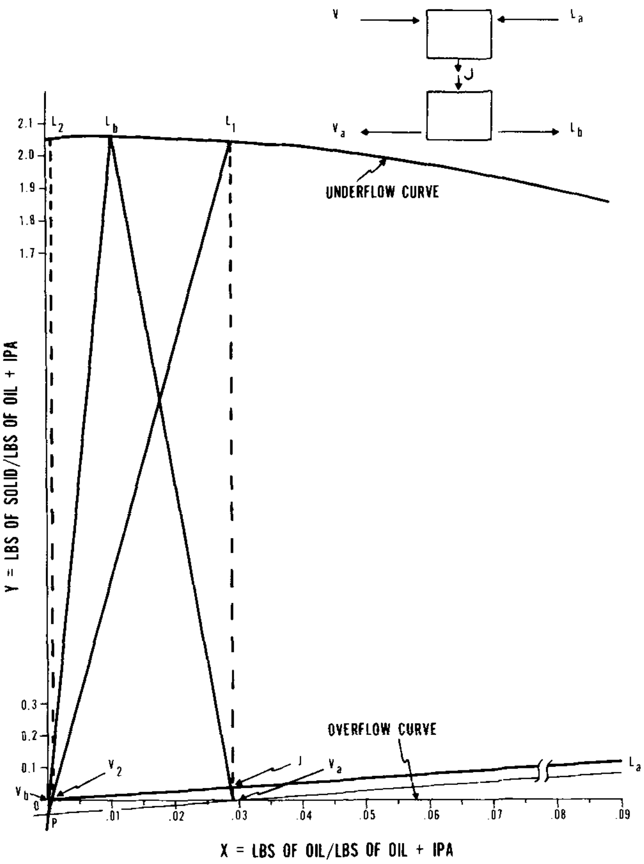

FIG. 5. Ponchon-Savarit construction for menhaden-isopropyl alcohol extractions at 60 C.

b) *The operating line:* An overall material balance can also be treated from a consideration of the underflow and overflow streams of stages of the countercurrent cascade. Therefore, if V_n+1 is defined as the inlet solvent to the nth stage and L_n as the exhausted solids from the nth stage, then a material balance over the first n stages gives: $V_n+1 = L_n+P$. The point P is described adequately by McCabe and Smith (10).

The operating line is represented by the above equation, and it is a straight line passing through the points P, V_n+1 and L_n. All other individual operating lines pass through point P, and these operating lines used alternatively with the vertical equilibrium lines give the Ponchon-Savarit construction shown in Figure 5.

To use the Ponchon-Savarit construction to determine the number of theoretical stages required to remove fat and water from menhaden having the "average" composition stated above, we must locate points on the operating line. First, points representing the raw fish L_a ($X = 1$, $Y = 1.39$), the solvent V_b ($X = 0$, $Y = 0$) and the desired underflow composition for the end point L_b are plotted on the X, Y diagram. To locate L_b for the desired level of 0.5% fat in the dried product, a line of known slope through the origin is plotted, and its intersection with the underflow curves locates L_b. The slope of this line is Y/X, which from basic definitions is: lb. solids/lb. oil ($1/0.005 = 200$).

The J point is obtained by the application of the center of gravity principle (lever rule for mass ratios) for a mixture of two streams. Thus the solvent-solid ratio is set by the minimum solvent ratio as previously calculated, and this solvent ratio together with the application of the center of gravity principle determines the J point. Next the stream

TABLE III

Theoretical Stages Required for the Isopropyl Alcohol (IPA) Extraction of Menhaden

Solvent	Temperature	Number of theoretical stages required
Azeotropic IPA	50	3
Azeotropic IPA	60	2
Azeotropic IPA	70	2
Anhydrous IPA	60	2

composition V_a is obtained by drawing a line through L_b and J and extending it to the overflow curve. Point P is then located from the application of the equation for the operating line, and the Ponchon-Savarit construction is completed. Thus we see that a second extraction is needed to bring the fat content of the FPC down to the desired level represented by L_b. A second extraction brings the fat content to L_2 which has the coordinates (0.00075, 2.05). The fat content of the dried product would then be 0.00075/2.05 or 0.04%.

A similar construction for the extraction of menhaden with IPA at 50 C and 70 C and for the extraction of menhaden with ethanol was carried out, and the results are summarized in Table III.

DISCUSSION

The extraction of oil and water from raw fish to produce FPC may not be strictly a leaching process for all stages. A portion of the oil and water is held so loosely by the initial raw protein that the first stage amounts to little more than a wash. Unsteady state conditions prevail, and regardless of how much solvent is used, within limits, removal of some water and a small amount of oil will take place when the mixture is separated by centrifugation. From the second stage on, however, leaching does occur.

Inspection of the data in Table I indicates that a low temperature (50 C) extraction with azeotropic IPA would require a significant increase in the solvent-solid ratio. This engineering analysis also suggests that 100% isopropyl alcohol is a better solvent than 87.7 w/w (azeotropic) IPA, and that ethanol was the poorest solvent. Ethanol, as a solvent for menhaden oil-water mixtures, requires solvent-solid that may be economically prohibitive.

These results agree with the work of Dambergs (11) who concluded that the maximum amount of lipid and the minimum amount of protein is extracted from herring by anhydrous IPA. Dambergs (12) also reports that "maximum extraction is achieved with diluted solvent containing about 22% water." This corresponds closely to the first stage water content for a countercurrent extraction of "average" menhaden with 100% IPA.

The effect of excess water in fresh solvent is severe. In the normal operation of a process unit producing FPC, the used solvent is purified and then recycled. In the purification step, oil and water are removed from the solvent mixture by centrifugation and distillation, respectively, and azeotropic solvent is normally reclaimed for reuse. However the above analysis indicates that wet IPA, due to inadequate distillation, will cause severe problems in the extraction and could result in a product with higher residual oil than required.

The data in Table III indicate that the number of theoretical stages required changes very little with temperature. This is probably due to the fact that the slope of the underflow line is very gradual and does not increase significantly with a change in temperature from 50 C to 70 C.

The minimum solvent ratio calculated above is the minimum solvent required in order to obtain a single phase extract solution. Therefore, if the designer wishes to avoid the presence of a separate oil phase in the extract solution, a high solvent-fish ratio is necessary. On the other hand, if the designer is willing to use a three-phase centrifuge to recover oil, miscella and solids, lower solvent-fish ratios are possible. However any reduction of solvent below the above calculated minimum solvent ratios requires a corresponding increase in the number of extraction stages. Optimization of the solvent-fish ratio to produce a product at the lowest cost is therefore desirable. The solvent-solid ratio to be used by the National Marine Fisheries Service in their Experiment and Demonstration Plant (13), where FPC will be made from fatty fish, is 2:1 using five stages plus a slurry mix tank and utilizing azeotropic IPA at a temperature of ca. 80 C.

The simplifying assumptions made in the material balance calculations are valid within the limits of engineering accuracy. Some solvent is retained by the solids after extraction, but the overall amount retained is so insignificant that the error involved is less than 2%. Some of the protein may be dissolved in the solution after extraction, but the amount dissolved is dependent upon the amount of free water available. The maximum amount dissolved is ca. 1.5% for azeotropic IPA, when a solvent-solid ratio of 2:1 is used.

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