Technical

Recovery of Water-Soluble Solvents from Oilseeds

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ABSTRACT

Water-soluble solvents such as ethanol and isopropanol are recovered from oilseeds in equipment similar to that used for recovering hexane, but the bases for design are considerably different. Present and future commercial processes employing aqueous solvents are described, and desolventizing extracted particulates from them examined, particularly as they are affected by the concentration of alcohol in the solvent.

INTRODUCTION

Among recoverable volatile solvents used for extracting particulates, aqueous ethanol and isopropanol have become commercially important in the oilseed industry. Desolventizing extracted particulates when the solvent is aqueous is more difficult than when the solvent is water immiscible because the solvent must be stripped from water as well as from oil. Although true phase equilibrium data is not available for designing desolventizing equipment, making useful generalizations is possible.

Oilseed processes proposed or in use that employ aqueous solvents follow. (a) Extraction of white (hexane-extracted) soy flakes with alcohols to improve product quality (1,2). The extracted flakes were flash desolventized to low residual alcohol in an unsuccessful effort to desolventize completely without steam stripping. Some alcohol appeared to be bound in the flakes. (b) Extraction of white flakes with 60-70% aqueous ethanol to produce soy protein concentrate (SPC). The flakes from this process are pressed and then desolventized, or the aqueous ethanol in the flakes is displaced with strong (more than 90%) ethanol (3) and the flakes desolventized without pressing. (c) Extraction of carbohydrates from full-fat flakes with 60-70% ethanol, followed by extraction of oil with 92% ethanol (4,5). From the standpoint of desolventizing, the extracted flakes are identical with the SPC washed with strong alcohol. (d) In nondistillation processes, by which oil is extracted from soybeans and cottonseed with strong ethanol or isopropanol, the oil is precipitated by cooling the miscella, and the alcohol phase is recycled to the extractor (6-9). In the past, researchers supposed that the flakes would have to be predried to prevent dilution of the recycling solvent, but in the most recent of these publications (8,9) the implication is that strongly pressed extracted flakes hold all of the water initially in the unextracted flakes. Although the residual solvent in strongly pressed flakes may be more dilute in alcohol than is the solution pressed from the flakes, that no net water leaves the flakes is unlikely. Experimental data is needed. (e) Extraction of aflatoxin from oil-free cottonseed flakes with strong ethanol or isopropanol (10). (f) Extraction of aflatoxin, gossypol, phosphatides and free fatty acids (FFA) from full-fat cottonseed with 85% ethanol, followed by extraction of oil with 92% ethanol (11,12).

DESOLVENTIZING METHODS

Recovering aqueous solvents from particulates is inherently more expensive and more difficult than recovering hexane. Because the solvent wets oilseed particulates, solvent content of extracted flakes, even after pressing, is much higher than the drained holdup in hexane-extracted particulates. Latent heats are much higher: 360 cal/g for 60% ethanol and 219 cal/g for 92% ethanol, compared with 79 cal/g for hexane. For recovering the last of the alcohol from the particulates, the alcohol has to be stripped from its dilute aqueous solution, which is more difficult than stripping hexane from residual oil.

When the solvent is immiscible with water (13), the particulates can be completely desolventized in a single step, either by countercurrent contacting with steam, or, if the particulates have a high water content, by boiling solvent and water from them. Neither of these is applicable to aqueous solvents. Contacting with steam increases the water in the particulates that must then be stripped; boiling a dilute solution is an inefficient way of stripping it. In another way of looking at the problem, the solids may be considered as the carrier of a solution of, say, 60% or 90% ethanol from which the ethanol is to be recovered. The most logical way to do so in the absence of the solids would be by evaporation followed by stripping in a column. The equivalent of an evaporator is a superheated vapor desolventizer or a schnecken; the equivalent of a stripping column is a deodorizer.

Superheated vapor desolventizing is not as attractive in this application as it is when applied to hexane. The molar heat capacity of 60% ethanol vapor is 12.4; of 92% ethanol, 12.9; of hexane, 34.4; of the mixture of 96% hexane and 4% water that circulates in a hexane vapor desolventizer, 30.2. For a given heat input, ca. twice as much volume of aqueous alcohol vapor as hexane vapor has to be circulated. Ca. 8.9 times as much volume of vapor must be circulated to boil 1.0 kg of 60% ethanol as to boil 0.96 kg of hexane plus 0.04 kg of water; and 4.0 times as much volume of 92% alcohol as hexane plus water.

Schneckens are relatively better. Because a high heat transfer coefficient is expected for alcohol evaporation, the heat transfer surface required for aqueous ethanol evaporation would be proportionately less than the ratio of latent heats. Perhaps recovery of the first of the solvent in schneckens at a very high heat transfer coefficient, followed by vapor desolventizing, is best.

Deodorizers of a design similar to that now used in hexane plants should suffice for stripping. However, they will have to be designed for more efficient contacting with steam than at present.

Vapor Desolventizing

The processes outlined above result in particulates to be desolventized that may be classified in 2 categories. (a) The solvent in the particulates contains ca. 60% ethanol. By moderate pressing, the solvent holdup is reduced to ca. 1 kg of solvent/kg meats. (b) The solvent in the particulates contains ca. 90% ethanol. Without pressing, the holdup is ca. 1 kg/kg meats.

Although no equilibrium data is available for the system liquid ethanol-liquid water-meats in contact with vapor, assuming that the effect of the solids is not profound is probably safe, so that the well-known phase diagram at atmospheric pressure for the liquid-vapor system, Figure 1, applies even if only qualitatively. What happens in a vapor desolventizer can be seen (14) from Figure 1.

Because the volume of vapor circulating in a vapor

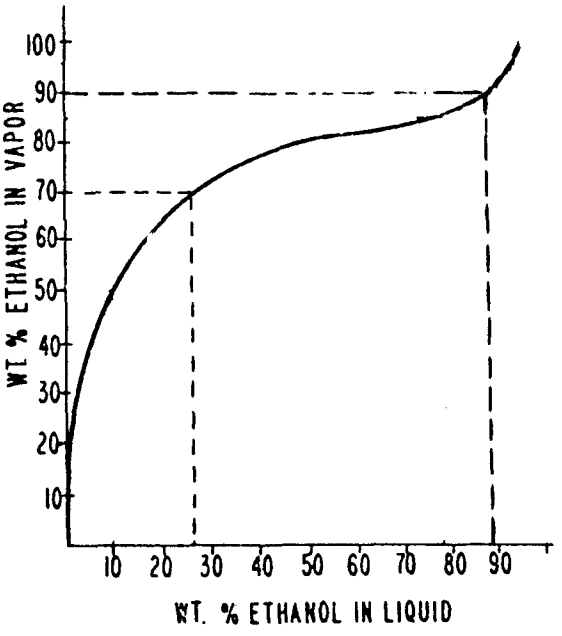

FIG. 1. Vapor-liquid equilibrium for ethanol-water solutions at 760 mm.

desolventizer is very large, the vapor composition does not change much as solvent vaporizes into the stream. The composition is that of the exiting vapor, essentially the same as the solvent composition. Suppose this is 70% ethanol by weight. The solvent in the flakes in equilibrium with 70% vapor contains 27% ethanol. Consequently, only ethanol vaporizes until the liquid composition is 27% ethanol; afterward ethanol and water vaporize to maintain the liquid phase at 27%. Suppose the solvent composition is 90% ethanol by weight. Liquid in equilibrium with a vapor of that composition contains 89% ethanol, so from the very beginning both alcohol and water vaporize. Two notable consequences arise from this situation.

Mustakas et al. (2) found that flakes containing aqueous ethanol with a concentration as high as 70% were completely denatured when flash desolventized, whereas flakes initially containing more than 90% ethanol were not denatured at all. This is now explained, because protein in flakes containing a 27% ethanol solution is very rapidly denatured at desolventizer temperatures, whereas protein in contact with 89% ethanol is not denatured.

Now suppose flakes containing 1.0 kg 70% ethanol/kg meats are vapor desolventized. Initially 0.59 kg of ethanol will be vaporized, at which point the residual solvent in the meats will consist of 0.11 kg ethanol and 0.3 kg water. This is an imprudent operation as the flakes at this point will be soft and sticky, and may well plug the desolventizer. Two possible remedies can be used. More dilute ethanol in the flakes can be displaced by strong ethanol before desolventizing, as shown by O'Hara et al. (3). Or a stream of vapor containing more than 90% ethanol can be fed into the vapor circulating in the desolventizer (14). That one of these expedients is used will be assumed in the remainder of this discussion.

To what residual ethanol content should the flakes be desolventized? Certainly not to as low a residual as possible, because the flakes will become brittle if dried. A practical basis might be to desolventize to a residual that on subsequent adiabatic stripping with steam the water content of the flakes would be 8% (0.087 kg water/kg meats). Suppose the solvent in the flakes leaving the desolventizer is 89% ethanol. After stripping, for each kg of ethanol vaporized, 0.42 kg of water is in the flakes. The ethanol content of flakes leaving the desolventizer is 0.21 kg/kg meats (0.087/0.42) or 17.4%. Alternatively, the water content desired in the flakes leaving the stripper might be as high as 12% (0.136 kg/kg meats), in which case the ethanol content of flakes leaving the desolventizer is 0.32 kg/kg meats, or 24.5%. An obvious advantage of desolventizing to 17.4% is that the desolventizer is only incrementally larger, at little extra cost, whereas the stripper is only ⅔ as large.

What is the temperature of the flakes leaving the desolventizer? Data for the calculation is not available, but the effect of having the meats in contact with the liquid should reduce the vapor pressure of the liquid by ca. 10%. That vapor pressure is further reduced by ca. 30% as a consequence of the very small cavities in extracted oilseeds is likely (13). The overall reduction in vapor pressure is 37%, so the temperature should be ca. 192 F, compared with 170 F, the boiling temperature of 89% aqueous ethanol. This may explain why Mustakas et al. (2) found high residual alcohol when they tried to desolventize completely in a flash desolventizer.

Stripping

Suppose flakes containing 89% ethanol and 0.01 kg oil/kg meats are to be countercurrently stripped with saturated steam. The solvent dissolves the oil in the feed, but the consequent reduction in vapor pressure is small. As the alcohol content of the liquid in the meats is reduced during stripping, oil falls out of solution and the solubility of solvent in oil becomes negligible. So, aside from the unknown effect on the phase equilibria of having meats in contact with the liquid, the deodorizer may be considered a column for stripping ethanol from water. If flakes are to be stripped to, for example, 200 ppm of residual alcohol (8% water basis), then the water leaving in the flakes may be considered to hold 2,500 ppm or 0.25% ethanol.

Figure 2 is the McCabe-Thiele diagram in log-log coordinates for this stripping,

$$\text{where } x_f = \left[\frac{89}{46}\Big/\left(\frac{89}{46} + \frac{11}{18}\right)\right] = 0.76$$

$$x_w = \left[\frac{0.0025 \times 18}{46}\right] = 0.001$$

and the steam fed is 1 kg/kg water in the stripped flakes. The equation of the operating line is $y = x - 0.001$. Even at

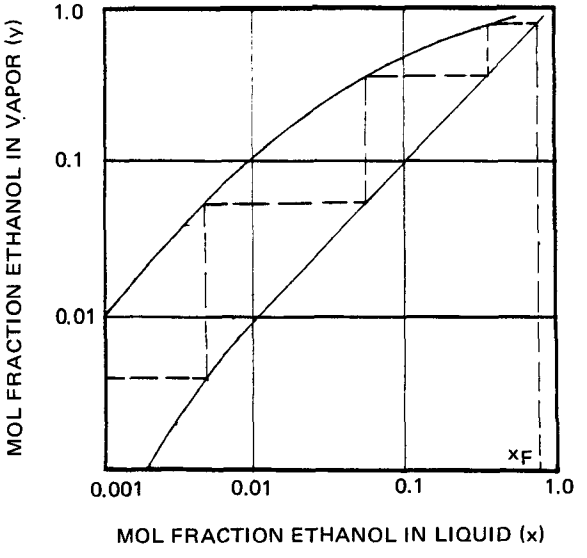

FIG. 2. McCabe-Thiele diagram for stripping ethanol from aqueous solution. $x_F = 0.76$, $x_W = 0.001$; 1 mole stripping steam per mole of bottoms.

this high steam rate, 3½ theoretical stages are required. Deodorizers designed for hexane stripping probably do not provide more than 2 theoretical stages. Alcohol strippers will have to do better, but they will probably not provide more than 3½ theoretical stages. The proposed steam flow of 1 kg/kg water in the stripped flakes is realistic.

Aside from possible reduction of protein denaturation, little advantage can be found for vacuum stripping, since the y-x diagram for ethanol-water is not sensitive to pressure.

DISCUSSION

As yet little commercial experience in recovering aqueous solvents from oilseeds exists. When equipment will be needed to do so, its design should be based on previous experience in the oilseed industry and on rational consideration of the properties of aqueous solvents and their interaction with oilseed components. Better physicochemical data are needed than is now available.

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Oil Content and Fatty Acid Composition of Peanuts Imported into Japan

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ABSTRACT

The oil content and fatty acid composition of Virginia, Runner, and Spanish market types of peanuts imported into Japan were determined. The significant differences among the countries of production were shown in stearic, eicosenoic and lignoceric acid contents of Virginia market type and oil content and palmitic, stearic, oleic, linoleic, eicosenoic, behenic and lignoceric acid contents of Spanish market type. The Spanish market type, as compared with the Virginia market type, was significantly higher in palmitic, stearic, linoleic, arachidic and behenic acid contents and lower in oleic, eicosenoic and lignoceric acid contents on the gross samples.

INTRODUCTION

In Japan, 38,550 tons of shelled peanuts (Virginia market type, 35,740 tons, and Spanish market type, 2,810 tons) were harvested in 1981. A total of 51,300 tons of shelled peanuts (Virginia market type, 21,000 tons, and Spanish and Runner market types, 30,300 tons) were imported in 1982. Thus, about 60% of the consumption depended on foreign trade. Imports were primarily from China and the U.S.A. for the Virginia market type, China and South Africa for the Spanish market type, and the U.S.A. for the Runner market type. About two-thirds of the world's peanut crop is crushed for oil. In Japan, however, peanuts are used mostly for food products: salted peanuts, peanuts roasted in-shell, confectionaries and peanut butter. As to the effect on products of fatty acid composition, high linoleic acid content decreases the shelf life because of a negative correlation between linoleic acid content and oil stability (1). The wider ratio of oleic acid to linoleic acid in peanut oil was considered as an indicator of more stable oil (2-4). From the standpoint of the nutrition, high linoleic acid content is desirable because the acid, in addition to being an essential fatty acid, has a hypocholesterolemic effect (lowering of blood cholesterol) (5). In previous studies, it was shown that the fatty acid composition of peanuts was affected by growing location in Japan, and the oil content and fatty acid composition were correlated with daily mean temperature during the ripening period (6). Holaday and Pearson (7) also reported the U.S.A. location where peanuts were grown significantly affected their fatty acid composition; and a significant correlation also exists between the mean temperature during the growth period and the level of major fatty acid contents. This suggested that the oil content and fatty acid composition of peanuts imported into Japan may vary by the countries of production because of different varieties and also different growth temperatures. Therefore, investigations were undertaken to study the oil content and fatty acid composition of peanuts imported into Japan.

EXPERIMENTAL

Materials

Three market type peanuts imported into Japan were collected in 1982. These were as follows: Virginia market type, 16 samples from 3 countries (China, U.S.A. and Australia); Runner market type, 5 samples of variety Florunner from the U.S.A., and Spanish market type, 37 samples from 8 countries (China, Thailand, Argentina, Paraguay, Brazil, Sudan, South Africa and Australia).

Analytical Procedure

Skins (seed coats) were removed and kernels were crushed in a mortar with a pestle. Oil was extracted from the crushed sample on a Butt type extractor with diethyl ether as a solvent. Fatty acids in the oil were determined by gas chromatography after transesterification to their methyl ester by the boron trifluoride method as outlined by the Association of Official Analytical Chemists (8). Esters were separated by using a Shimadzu GC-6APF chromatograph equipped with a FID and 3 mm × 3 m glass column packed with Unisol 3000 Uniport C, 80-100 mesh (Gasukurokogyo Co., Ltd.). The column temperature was 240 C, and the