Technical News Feature

Recovering Water-Immiscible Solvents from Oilseeds

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ABSTRACT

Processes used in desolventizing are reviewed. Anomalous high residuals in desolventized, deodorized and toasted flakes can be accounted for by assuming that the dimension of void spaces in flakes after extraction of oil is about 10^{-6} cm, with consequent substantial reduction in vapor pressure.

INTRODUCTION

After the extraction of particulate solids by a volatile, combustible or valuable solvent, quantitive recovery of solvent from the spent particulates is mandatory. Since solvent extraction has its most important application in the oilseeds industry, the technology of particulate desolventizing has been developed there. Most applications employ hydrocarbon solvents, particularly commercial hexane. The rules applying to chlorinated solvents are essentially the same. Water soluble solvents, such as ethanol and isopropanol, are being used increasingly. They will be treated in a later paper.

Substantially complete desolventizing may be accomplished in a single step, but generally the bulk of the solvent is removed in a first step and the remainder stripped in a second step.

Solvents immiscible with water may be stripped from particulates in a single step in two ways:

- First, the solvent wet particulates are countercurrently stripped with saturated steam. The bulk of the solvent is evaporated quickly at the particulate feed end of the stripper, and an equivalent amount of steam is condensed on the particles. The remainder of the solvent is more slowly stripped from the particulates as they move the length of the stripper, the rate decreasing as the solvent content of the particulates diminishes. Desolventized particulates are wetter than the feed.
- Second, if the particulates contain enough inherent water, they can be freed of solvent as they move along a path in which they are heated indirectly. At first, the solvent vapor and steam that are generated approximate in their proportions that of the azeotrope. As the solvent in the particulates is depleted, the vapor generated has less and less solvent. If enough water is boiled, this should be a very effective way of achieving substantially complete desolventizing, since it does not depend on bringing the particulates into intimate contact with steam. Desolventized particulates are drier than the feed.

In each of these cases, the minimum theoretical steam required is that needed to boil the azeotrope, not just the solvent. If the particulates are initially free of water, it is usually better to vaporize the bulk of the solvent with indirect heat.

The following are the combinations employed in two-step processes:

1. Most of the solvent is vaporized by indirect heat; the last of the solvent is stripped by countercurrent saturated steam. This is exemplified by the combination of vapor or flash desolventizer and deodorizer.
2. Most of the solvent is vaporized by condensation of steam on the particulates; the last of the solvent is distilled, along with water, by indirectly heating the particulates. This is exemplified by the D-T.

VAPOR OR FLASH DESOLVENTIZING

Early oilseed plants used jacketed screw conveyors (schneckens) for desolventizing. These were replaced by vapor or flash desolventizers employing direct contact of the particulates with a circulating stream of superheated solvent vapor, first proposed by Leslie (1). The system he patented, Figure 1, comprised a horizontal vapor desolventizer through which the particulates are conveyed by a rotating cage which has a conveying scroll and lifting flights. In the patent drawing the superheated vapor enters at the middle of the desolventizer and flows in both directions, cocurrent and countercurrent to the flakes.

Down to a residual solvent in the flakes of about 2%, desolventizing is rapid. A flash desolventizer works as well as the vapor desolventizer. The vapor desolventizer has two advantages.

It makes less fines, and a flash desolventizer has no surge capacity to provide against even a momentary slug of excess solvent in the feed, whereas the vapor desolventizer, with about 10 min retention time, can handle an overload of short duration. In this regard, neither is as good as a schnecken, which responds to a slug of solvent with an increase in heat transfer coefficient.

In any case, the particulates cannot be heated to a temperature much above the azeotrope boiling point as long as they contain more than about 2% residual solvent, even though they may be in contact with vapor whose temperature is in excess of 300 F. Consequently, there is little loss of protein solubility during vapor desolventizing.

Superheated vapor desolventizing is particularly applicable to hydrocarbons like hexane, whose vapors have a high molar heat capacity, equivalent to a high volumetric heat capacity. The superheated vapor is circulated by a constant volume blower and heated to a constant controlled temperature, so the sensible heat added in unit time is proportional only to the molar heat capacity. The specific heat of hexane vapor is 0.5, its molecular weight 86; the molar heat capacity is 34.4. Contrast this with water vapor, whose

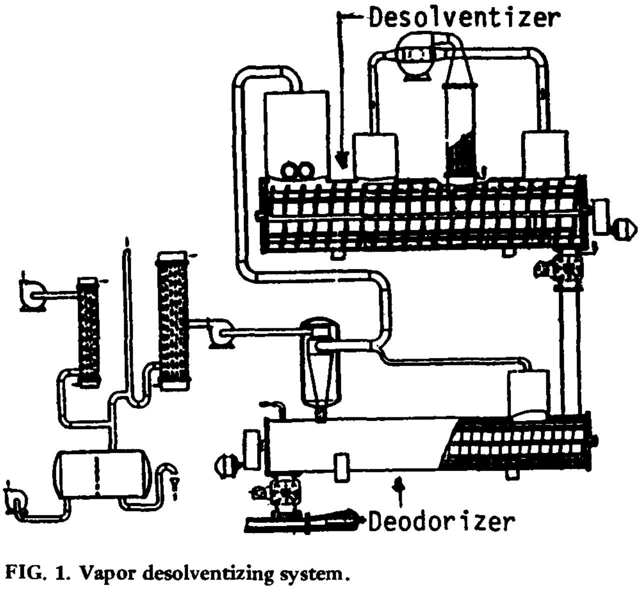

FIG. 1. Vapor desolventizing system.

specific heat is 0.48, molecular weight 18; molar heat capacity 8.6. It is important to keep steam from leaking into a vapor desolvenizer, say from the deodorizer, since the system's desolventizing capacity is reduced seriously by adding steam to the circulating vapor.

DEODORIZING

Following vapor desolventizing, the particulates are stripped to a low residual solvent content by countercurrent contacting with saturated steam. The term "deodorizing" was coined in 1944 by the late E. H. Leslie to emphasize that an excess of steam might well improve the flavor of stripped soybean flakes. A deodorizer is most often a horizontal vessel with a rotor in it designed to convey and shower the particulates during a retention time of about 15 min.

In the bad old days, there was no particular basis for deodorizer design, since it appeared easy to strip to the 500 or so ppm of residual solvent in the flakes required to meet solvent loss specifications. When I designed a deodorizer in 1946, I had no better basis, so I used enough steam (about 5 lb/100 lb of flakes fed to the deodorizer) to give a vapor velocity high enough to assure that the steam would flow countercurrent to the flakes without back-mixing. Now there is atmospheric pollution to be considered. When a low residual solvent is required, deodorizing may be considered primarily as stripping the residual oil to a low residual solvent content. As will become apparent, residual oil content is paramount in its effect on residual solvent.

Deodorizing may be carried out under vacuum if protein solubility is to be preserved, at atmospheric pressure, or at superatmospheric pressure to toast at the same time. It is a fallacy that under all circumstances deodorizing is easier under vacuum. If considerable excess steam is used, the partial pressure of hexane in the exit vapor is small, so the equilibrium partial pressure of hexane over its solution in oil becomes the driving force. Deodorizing temperature is essentially the saturation temperature of wet flakes in contact with steam, about 223 F at atmospheric pressure. Since this temperature increases with pressure, and hexane equilibrium partial presence increases exponentially with temperature, it should be easier, in the presence of excess steam, to deodorize under pressure. Also, diffusion is faster at high temperature.

DESOLVENTIZING-TOASTING

In the D-T in common use, flakes from the extractor are contacted with steam to evaporate almost all of the solvent and simultaneously condense enough water on the flakes to increase their moisture content to about the 20% needed for toasting. Next, some of this water is boiled from the flakes as they are conveyed over the heated trays of the D-T, and it is expected that the steam generated will complete the stripping of hexane from the flakes. The rest of the condensed water is evaporated in a separate drier.

Before their protein is denatured, flakes with a water content of 20% readily form water balls. Consequently, the flakes are handled gingerly in the zone of initial contact with steam; contacting is poor, and steam is wasted, as evidenced by the high temperature of the hexane-steam mixture leaving the D-T, normally about 180 F instead of the theoretical minimum of 140 F. In present practice, the excess steam is not wasted entirely, since the D-T vapor is used to heat the first stage of miscella evaporation.

Before the D-T came into wide use, I disclosed (2) that the same process might be carried out by feeding as process steam only the amount of steam leaving with the exit vapor, but not the steam that condenses on the flakes. The apparatus is shown in Figure 2, taken from the patent. A Rotocel extractor is mounted on a vertical tank, through which extracted flakes discharged from the Rotocel descend over a succession of disc- and doughnut-raked trays. After initial trays on which the intermittent discharge from the Rotocel is converted to steady flow, the flakes are efficiently, countercurrently contacted with steam ascending from below. Next, by retention on heated trays the flakes are toasted and simultaneously dried by boiling water from them. At the time the invention was made, plants were smaller than now and toasting times were longer, so it was deemed practical to do all of the drying within the desolventizer-toaster.

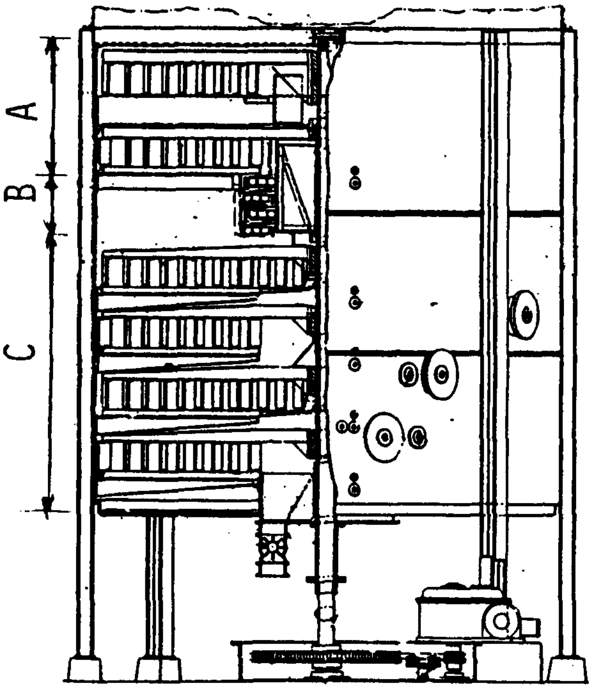

FIG. 2. D-T system for minimum steam consumption. A, flow smoothing trays; B, desolventizing trays, and C, toasting-drying trays.

In present practice, only a small amount of the drying is done in the D-T and the rest done in a separate steam-tube drier. Heat in the water vapor leaving the drier is lost. In a recent patent (3), Hansotte draws no air into the dryer and pipes the water vapor leaving it to the D-T, preferably blowing the vapor to avoid having to put the dryer under pressure. The motive for doing this is not primarily to save steam, but to recover solvent from flakes leaving the D-T in order to meet atmospheric pollution standards.

COMMERCIAL DESOLVENTIZING EXPERIENCE

The following is the commercial experience: There is more solvent than expected in the flakes leaving the vapor desolventizer; deodorizers work reasonably well, but do not always deliver flakes with low residual solvent, and desolventizer-toasters do a poor job of desolventizing. Residual hexane in exiting flakes frequently is in excess of 500 ppm.

How much residual solvent is expected? Solvent in the flakes leaving a vapor desolventizer may be estimated as follows: Hexane is in the flakes dissolved in residual oil and as vapor in the voids. Since desolventized soybean flakes have 40% voids (4), hexane in the vapor is a surprisingly large portion of the total. If flakes leave the desolventizer at 170 F and one atmosphere containing 12% water and 1% oil (hexane-free basis), the vapor pressure of water over the flakes is 210 mm, and the equilibrium partial pressure of hexane (by difference) is 550 mm. The hexane-oil solution in equilibrium contains 0.23 gm hexane per gm oil or per

100 gms of flakes. The void volume is 51 ml per 100 gms of flakes; at 170 F these voids hold 0.00228 gm moles [(51 × 492)/(22400 × 630)] of which 0.00165 mole [(0.0028 × 500)/760] or 0.14 gm, is hexane. Total residual hexane expected is 0.37%. Experience is that it is much more.

Similar reasoning can be applied to deodorized or toasted flakes. When a flake is suspended in steam, heat transfer is much more rapid than mass transfer and the flake quickly comes to its temperature in equilibrium with steam, 223 F at atmospheric pressure. The driving force for hexane evaporation is enormous, so even in the absence of diffusional transfer in the deodorizer or of purging of hexane by steam generated in the D-T, residual hexane would be expected to be negligible. It is not.

A PLAUSIBLE EXPLANATION

There is, possibly, a simple explanation. It is known that vapor pressure in small cavities is reduced, provided that the radius of the cavity is less than 10^{-6} cm (5). The cavities in oilseed flakes are intracellular and may well be this small, particularly those left by the extraction of oil droplets. It is plausible that the equilibrium partial pressures of water and hexane may be reduced by 30%, with remarkable effect on calculated residual hexane.

The vapor pressure of water in the cavities of a flake at 170 F immediately after desolvenitizing, particularly in a flash desolventizer, is now 147 mm (0.7 × 210). The partial pressure (by difference) of hexane is 613 mm; and adjacent to the cavities the hexane solution in oil, whose hexane concentration corresponds to an equilibrium partial pressure of 876 mm (613/0.7), contains 1.50 lbs hexane/lb oil. Since the total internal surface of the cavities is much larger than the external surface of the flake, this may be taken as the hexane concentration in all of the oil. Hexane in the cavities is 0.19 gm [(0.00228 × 613 × 86)/760] per 100 gms of flakes. Total hexane is 1.69% of the flakes.

The foregoing calculation assumed a dynamic non-equilibrium condition. Alternatively, as in a vapor desolventizer with retention time, the flakes may come to equilibrium with the circulating vapor, and the partial pressures of water and hexane in the cavities will be the same as in the vapor surrounding the flakes. Hexane and water must migrate to the interior of the flakes; the flakes' surface will be dry, and the partial pressure of water in the recirculating vapor reduced. In 1946, I sampled the vapor recirculating in the first vapor desolventizer at Allied Mills in Taylorville, Illinois, and found that the vapor contained 4% water, corresponding to a water partial pressure of 126 mm. The calculation still applies.

A similar calculation can be made of the hexane in a flake in dynamic contact with atmospheric steam. The temperature of the flake will be that of its external surface in free contact with the steam, 223 F. The partial pressure of water vapor in the cavities is 532 mm (0.7 × 760); partial pressure of hexane (by difference) is 228 mm; and the hexane content of a hexane-oil solution in contact with hexane vapor at a partial pressure of 326 mm (228/0.7) is 0.038 gm per gm oil or per 100 gms of flakes. Hexane in the cavities is 0.042 gms [(51 × 492 × 288 × 86)/(22400 × 683 × 760)] per 100 gms flakes. Total hexane is 0.080% or 800 ppm.

Consequently, additional hexane removal is required. Diffusional transfer to steam, as in a deodorizer, should work, by the following reasoning: Most of the oil in soybeans is relatively easily extracted. Slow extraction of the last of the oil can be ascribed to phosphatide interference. In fact, if extracted flakes are reimpregnated with oil, all of it extracts rapidly. About 90% of the oil is extracted in less than 3 min. Since diffusivity of gases is about 10^4 times that of liquids (6), transfer of hexane vapor from the flakes should be very rapid.

Blocking rapid transfer, however, is the immediate accumulation of water at the surface of each flake. Heat required to warm 100 lbs of flakes from 170 to 223 F and to boil 1.46 lb (1.50-0.038) of hexane amounts to 2210 BTU, corresponding to the condensation of 2.3 lb of water. As stated earlier, heat transfer to and in the flake is far more rapid than mass transfer, so the water condenses at the surface and the interior is heated by conduction. Access of steam to the interior may have to await redistribution of water in the flake (tempering), a much slower process than gas diffusion.

For the same reason, the heating trays of a D-T are not efficacious for stripping hexane. Steam-sparged flakes are noticeably very wet at the surface, so there can be little access of steam to the cavities. When only a small percentage of water is boiled from the flakes, the surface remains completely wetted. Only after additional drying can diffusional transfer occur. The Hansotte invention should do the job. Alternatively, flakes from the D-T could be flashed to as low a pressure as practically possible, although this probably would not reduce hexane to as low a residual as would drying followed by diffusion.

VACUUM vs. PRESSURE DEODORIZING

Vacuum vs. pressure deodorizing now can be reexamined. Diffusional gas transfer rate is not governing, since diffusion is very rapid even at the low temperatures corresponding to vacuum. Hexane content of flakes in contact with steam prior to diffusional transfer and amount of water condensed increases with pressure, as is illustrated by Table I derived from calculations similar to those already illustrated for 760 mm.

The advantage is clearly with vacuum deodorizing on both counts.

Another parameter that now can be examined more correctly than before is the steam required for stripping to a residual hexane of, say, 100 ppm. Since stripping to this low residual is a slow process, it would be unrealistic to assume that the minimum steam required for deodorizing will be less than the amount that corresponds to, say, two theoretical stages. Figures 3 and 4 show material balances for one and two theoretical stages operations at 350 and 760 mm abs. respectively. By the definition of a theoretical stage, in each stage materials and heat balance, the phases leaving are in equilibrium and partial pressures in the cavities are the same as those at the surface of the flake. Since it also is assumed that equilibrium water and hexane partial pressures in the cavities are reduced by 30%, it follows that a partially stripped flake at equilibrium has higher water and hexane contents in the interior than at the surface.

TABLE I

Effect of Increasing Pressure on Hexane Content of Flakes in Contact with Steam

Deodorizing pressure mm abs.	Maximum deodorizing temp. °F	H_1	H_2	H	W
350	189	210	210	420	1.1
760	223	380	420	800	2.3
1275	246	490	690	1180	3.4

H is total hexane content of desolventized flakes in contact with steam, ppm. H_1 is the hexane in the meats, ppm. H_2 is the hexane in the cavities, ppm. W is lbs water condensed per 100 lbs of desolventized flakes.

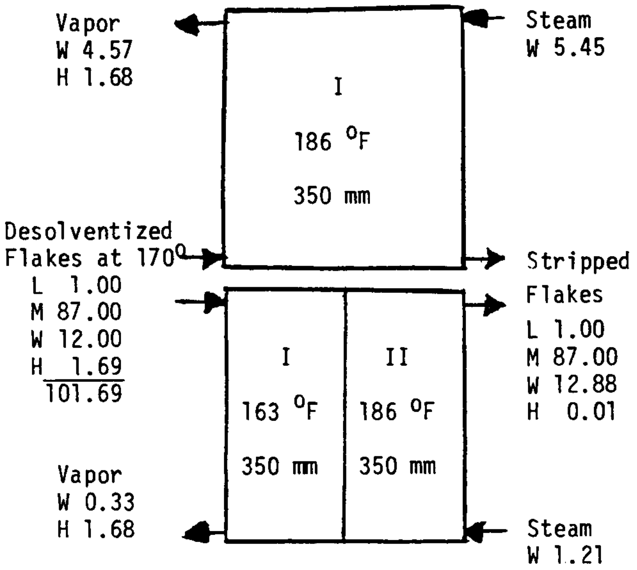

FIG. 3. Material balance for stripping to 100 ppm residual hexane in 1 and 2 theoretical stages at 350 mm abs. L = oil, M = meats, W = water, and H = hexane.

It is plain from these diagrams that:

- In either 1- or 2-stage operation, there is a substantial steam saving when vacuum is used.
- The steam saving in 2-stage vs. 1-stage operation is so large that there is no excuse for designing for less than the equivalent of 2-stage operation. Steam in the deodorizer must flow countercurrent to flakes.
- Unless the deodorizer provides more than 1 theoretical stage, the 5 lbs of steam per 100 pounds of desolventized flakes now used commercially will not suffice.

OTHER OILSEEDS

The theoretical equation for the reduction of vapor pressure in a small spherical cavity in a liquid is (5):

$$\frac{\ln p}{p_o} = \frac{2\gamma M}{r\rho RT}$$

where M is molecular weight of the liquid,
p is vapor pressure in the cavity,
p_o is vapor pressure over a flat surface,
r is the radius of the cavity,
R is the gas constant,
T is absolute temperature,
γ is surface tension and
ρ is liquid density.

(In cgs units, γ is expressed in dynes/cm and R = 8.314 × 10^7 ergs/degree/mole.)

Although the entire equation may not be useful in predicting actual vapor pressure reduction in cavities in oilseeds, some speculation is useful. Clearly the per cent of voids is greater in unpressed oil seeds whose initial oil content is higher than that of soybeans, but the cavities may be the same size. Pressing undoubtedly reduces the per cent voids and the size of the cavities.

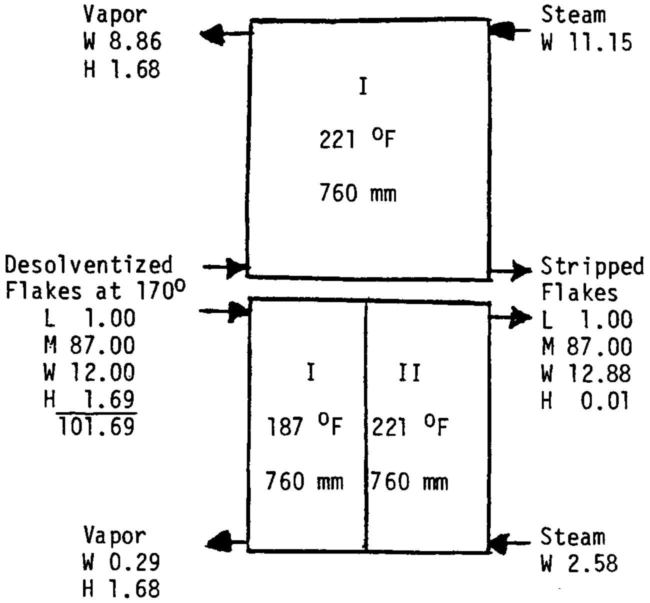

FIG. 4. Material balance for stripping to 100 ppm residual hexane in 1 and 2 theoretical stages at 760 mm. L = oil, M = meats, W = water, and H = hexane.

Suppose that desolventized flakes of an unpressed oil seed (cottonseed, perhaps) contain 50% voids (76.5 ml/100 gms flakes) and that the effective cavity size and other properties are the same as those of soybeans. Suppose that desolventized prepressed flakes of the same seed contain 30% voids (33 ml/100 gms flakes) and that the typical spherical cavity has 50% the volume of the typical soybean cavity (that is, its radius is 0.794 that of the soybean cavity). Using the same methods as before, here is how the hexane contents of flakes suspended in steam at atmospheric pressure compare:

	H_1	H_2	H
Soybeans	380	420	800
Unpressed seed	380	634	1014
Pressed seed	4500	620	5120

Prepressing undoubtedly increases considerably the difficulty of desolventizing.

REFERENCES

1. Leslie, E.H., U.S. Patent 2,571,143, Oct. 16, 1951.
2. Karnofsky, G., U.S. Patent 2,811, 539, Oct. 29, 1957.
3. Hansotte, R.J., U.S. Patent 4,332,092, June 1, 1982.
4. King, C.O.; D.L. Katz and J.C. Brier, Trans. Am Inst. Chem. Engrs. 40:533 (1944).
5. Glasstone, S., Textbook of Physical Chemistry, 2nd Edition, D. Van Nostrand Company, 1946, pp. 495-496.
6. Treybal, R.E., Mass Transfer Operations, McGraw-Hill Company, Inc., 1955, Chap. 1.

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