Liquid-Liquid Extraction

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LIQUID-LIQUID extraction is the application of partial solubility to the separation of liquid mixtures of two or more components. Liquid-liquid extraction processes are applied, in general, to the separation of mixtures which cannot be resolved by distillation for one or more reasons: a) distillation temperatures are too high; b) relative volatilities are too small or azeotropes exist; c) separation basis volatility is not satisfactory, *e.g.*, when a type separation is wanted. Presumably any mixture can be separated by extraction if its components differ from one another in molecular weight or molecular type. It is only necessary to find a solvent with which the mixture is partially miscible and in which one component or one type is more soluble than the other. The behavior of mixtures with solvents is probably a familiar subject, but, so that subsequent discussion will be generally understood, a brief description of common systems has been included herein.

Figure 1 is a plot showing the conditions of miscibility for a hypothetical solute and solvent. This type of diagram is useful in determining the conditions under which a separation must be made. Suppose a mixture of solvent and solute designated by the point X were to be dealt with. Separation could be made at any temperature lower than T_m but the amount of raffinate and extract will be proportional to XE and XR respectively. By changing the amount of solvent, T_m, XE and XR can be changed, but as long as T is constant, the composition of the two layers will be represented by *R* and *E*.

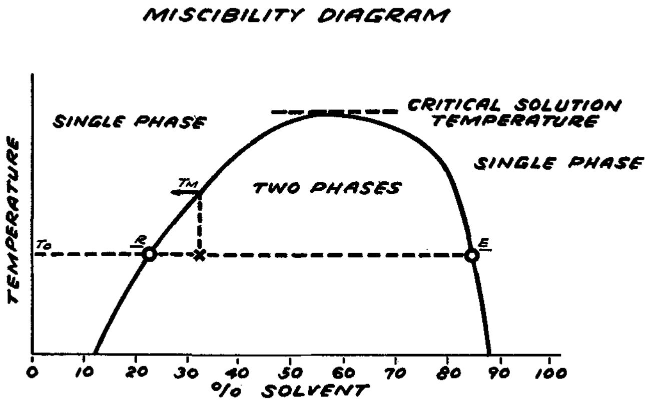

Fig. 1

If the solute consists of two components which are mutually miscible but each of which is only partially miscible with the solvent, the phase relationship may be represented by a triangular diagram, Figure 2. Other forms may exist in which there is only one single phase region, but the diagram shown is more typical.

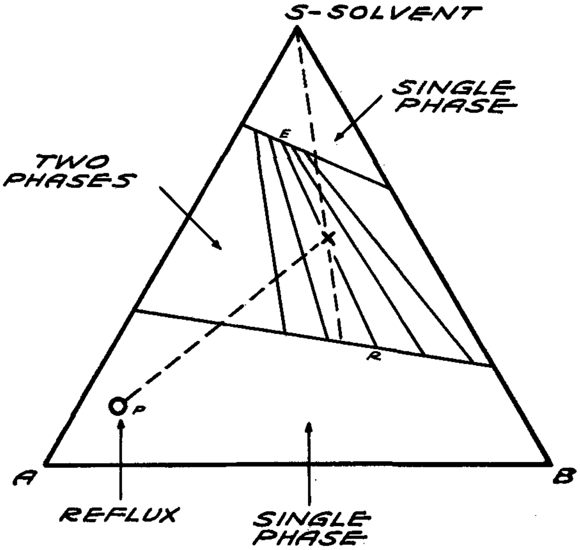

Fig. 2. Three component phase diagram.

This is an isothermal diagram, but a triangular prism, of which this is one slice, could be built with temperature as the vertical axis. Tie lines for the two-phase region connect the raffinate and extract phases, which are in equilibrium. The quantity of raffinate and extract are proportional to XE and XR respectively, and in this diagram the compositions of the phases can be obtained from the points at the ends of a tie line, such as ER. As long as the point X remains on a particular tie line, *E* and *R* are not changed. It can be shown that removal of part of one phase simply moves *X* along the tie line and therefore does not change the composition of either phase.

Addition of solvent changes the point X along the line XS, which crosses the tie lines and thus changes the composition of extract and raffinate. Note that the raffinate is caused to move toward the B-S axis to a greater extent than the extract is moved in the same direction. This simply means that a more selective separation is being made. Also note that, if too much solvent is added, a single phase can result.

Suppose that a reflux stream consisting of nearly pure A mixed with a small amount of solvent were added and that this diagram represented the condition existing in the extract end of a counter current system. Point X, representing the total system, would move toward P along XP, crossing tie lines and making the extract richer in component A, but if too much reflux is added, X crosses the phase boundary and no separation is made.

If it is not convenient to analyze the phases or if the system is multicomponent, it may be possible to represent the solute part by means of some convenient physical property, such as gravity or refractive index. This device is often used in complicated systems, such as petroleum and glyceride oils or fats. It should be used with great care because it involves some dangerous assumptions when applied to engineering calculations.

A special case could be encountered in that the components of the feed were not mutually miscible with each other or with the solvent (Figure 3). In this case three phases could occur. If, by chance, this condition occurred in an extraction system and it were not discovered phase *A* could be withdrawn as extract and either *B* or C as raffinate, depending on the densities, and the remaining one left in the system. The third phase would accumulate until the system was full of it, and then one product would seem to change abruptly as the third phase spilled over with either raffinate or extract. Obviously the chance selection of a three-phase system would be rare, and this is not to be assumed to be the cause of most upsets in extraction runs. However it is well to bear in mind that it could happen.

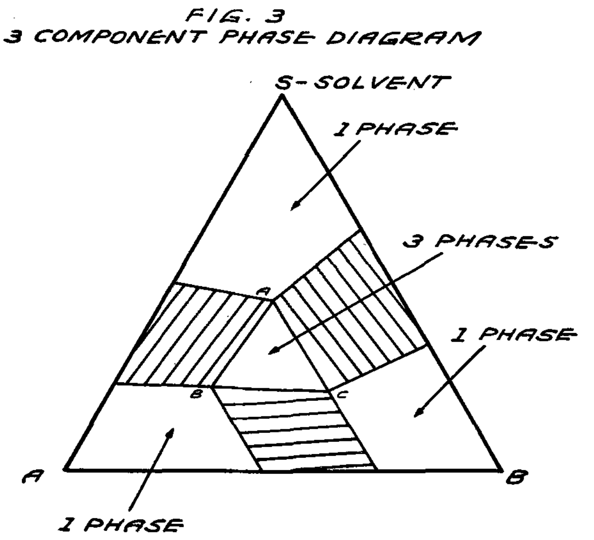

FIG. 3

Consider a mixture of solvent and solute which are not miscible, such as a simple, single-stage system in which such a mixture has been thoroughly agitated and allowed to settle. In engineering a liquid-liquid extraction system, we are chiefly concerned with the composition of the two liquid phases and how the differences in composition between them can be put to use in separating the components of the solute.

When the two liquid phases are in equilibrium, solute and solvent molecules are continually passing through the interface in both directions at rates determined by their relative concentrations and the physical conditions existing. These rates determine the equilibrium concentrations of the components of the phases. If any change of composition takes place in either phase, the diffusional rates will be unbalanced until a new equilibrium is established.

Since the components of the feed are mutually miscible in all proportions, increasing the concentration of the solute in the solvent phase makes the solvent phase become more attractive to the less soluble components of the feed, that is to say, the selectivity is reduced. Thus reducing the ratio of solvent to feed and maintaining a given extract yield invariably reduce the selectivity, or the ability of the solvent to distinguish one type of molecule from the other. There are several ways to improve the selectivity of a solvent, such as changing the temperature, adding water, etc., but these invariably reduce solubility of extract in the solvent.

Countercurrent Solvent Extraction

It has been pointed out briefly that solvent extraction is a diffusional process. Phase composition equilibria are reached by mass transfer of molecules across the interface from one phase to the other. If the phases are not in equilibrium, the transfer rates become unbalanced, resulting in net accumulation of components in one phase and depletion of the other in the direction of equilibrium.

Suppose the single-stage system were changed to two or more stages, solvent being introduced into one stage and feed to another, allowing extract and raffinate phases to flow in opposite directions and leaving at opposite ends of the system. The two solutions entering a given stage would not be in equilibrium. Mass transfer of components would take place with accumulation of more soluble components in the extract, and less soluble components in the raffinate, *i.e.,* compositions would change in the direction of equilibrium.

Since the densities of the phases are different, the multistage effect can be obtained by introducing solvent and feed at opposite ends of a vertical vessel or tower. The denser phase will flow countercurrently to the lighter phase. The concentration of components in the two phases in contact will not be in equilibrium, and mass transfer will take place, concentrating the more soluble materials in the extract phase and the less soluble ones in the raffinate phase.

The system now has the appearance of a distillation column, and since both are diffusional countercurrent processes, there should be at least some similarity. Distillation is a process which has been extensively studied, and its fundamentals are well known. Extraction, on the other hand, is fundamentally complex, and relatively little fundamental work applicable to multicomponent systems has been done. It should be realized that distillation can be and generally has been studied with fundamental laws of ideal mixtures as a basis for examination of data. This cannot be done for extraction. Solutions which obey or approximate the laws for ideal solutions are never encountered in extraction. Ideal solutions do not separate into two phases. Non-ideality is a prerequisite for a solvent extraction system.

In order to understand what is going on in an extraction tower, it is helpful to examine the analogy between extraction and distillation. For this purpose consider the following relationship:

Distillation	Extraction
Heat	Solvent
Liquid	Raffinate phase
Vapor	Extract phase
Rectifying section	Part from feed to extract end
Stripping section	Part from feed to solvent inlet
Theoretical tray	Theoretical stage
(Packed) HETP distance between liq. & vapor in eq.	HETS (distance between raff. and ext. in equil.
Reflux-condensed vapor (less heat) returned to tower	Reflux-solvent poor extract returned to tower

In this analogy solvent is called the analog of heat. In distillation, heat introduced in the reboiler or with the feed is the agency which causes the phases (vapor and liquid) to separate. In extraction, solvent causes the separation. The heat-rich phase in distillation is the vapor. The solvent rich phase is the extract. The vapor contains the concentrated volatile components. The extract contains the concentrated soluble components. The more heat introduced, the more vapor formed; the more solvent introduced, the more extract produced.

The stripping section of a distillation column is that part between the reboiler and the feed tray. In this section the liquid contains less of the more volatile components than does the feed. Heat is applied at the end of the stripping section to vaporize as much as possible of the volatile components. Throughout the stripping section the reboiler vapor exchanges its least volatile components for the more volatile components of the liquid.

The stripping section of an extraction column is that part between the solvent inlet and the feed point. In this section the raffinate contains less of the more soluble components than does the feed. Solvent enters at the end of the stripping section to dissolve as much as possible of the soluble components. Throughout the stripping section the extract exchanges its least soluble components for more soluble components of the raffinate.

The rectifying section of a distillation column is that part of the column between the reflux inlet and the feed point. In this section the vapor is richer in volatile components than was the feed. A part of the product is returned to the end of the rectifying section as reflux. The reflux exchanges its more volatile components for the less volatile components of the vapor.

Similarly the rectifying section of an extraction column is that part between the reflux inlet, or origin, and the feed point. The extract in the rectifying section is richer in more soluble components than was the feed. The reflux exchanges its more soluble components for the less soluble components of the extract. The two sections are not independent in either process. The compositions of fluids entering each part are influenced by the performance and conditions in the other.

Everyone is familiar with the fact that distillation systems can be defined by a material balance and a heat balance. Similarly solvent extraction systems are defined by a material balance and a solubility balance. If conditions are set up so that such a balance is not satisfied by the solubilities, a part of the feed will accumulate in the tower with eventually disastrous results.

Reflux in solvent extraction can be obtained in a manner similar to that generally found in distillation, *i.e.*, the extract product can be entirely or partially stripped of solvent and returned to the extract end of the tower. In distillation the vapor is condensed, that is, heat is removed and is pumped back to the vapor end of the tower. In distillation increased reflux means increased heat duty on the reboiler to satisfy the heat balance. In extraction increased reflux means that more solvent will be required to satisfy the solubility balance.

Reflux can be obtained in other ways with results which may or may not be better than the method described. Advantage can be taken of change in solubility with temperature by operating with a temperature gradient. If solubility increases with increasing temperature, the extract end is run colder than the raffinate end, thus reducing solubility and returning that part of the extract to the column as reflux. This is the analog of the partial condenser reflux system. Solubility can be changed with good effect in some systems by adding an adulterant to the extract phase, which reduces extract solubility, thus throwing out some of the less soluble components and returning them as reflux. Such systems are represented by phenol extraction of petroleum in which addition of water produces reflux.

All reflux systems must satisfy the solubility balance, or an unsteady state will be developed, resulting in eventual upset. Furthermore reflux is not always beneficial. Returning to the phase diagrams of the earlier discussion, the use of reflux is equivalent to adding more oil to the system, thus moving the point representing the system toward the miscibility line. If too much reflux is used, the point will cross this line, resulting in total miscibility and loss of phase separation. Under these conditions the products will tend to approach the feed composition.

Even though actual miscibility is not immediately encountered, it must be remembered that increasing oil concentration in the extract phase generally reduces selectivity of the solvent. If the selectivity loss is great, it may counter-balance the effect of the rectifying stages, and the separation will be poorer than could be obtained with no reflux at all. There are actually a number of instances where solvent extraction systems have been operated so close to miscibility, *i.e.*, minimum solvent, that elimination of reflux improved their performance.

Correlation of pilot plant data on the extraction of soybean oil to separate high and low iodine number fractions showed that increasing reflux above a certain point actually gave poorer results. Similarly increasing temperature gradient above 5°F. (at feed to extract) gave poorer results. Similar results were obtained by Lever Brothers in the solexol (propane) refining of tallow (1).

With the foregoing in mind the process engineer will proceed to design an extraction system for a given job. The first requirement is to know how high the tower must be and what type of internals are required. To decide this it is necessary to know the number of perfect stages of extraction required to make the separation with the amount of solvent which can be used, or conversely the amount of solvent it will take for the kind of tower which can be built.

The determination of the number of stages in simple systems is not difficult. A few equilibrium determinations can be used to establish plots similar to McCabe-Thiele diagrams, on which stages can be stepped off like trays. In the more complex systems, which are generally encountered in practice, the equilibrium data are not so useful and in many instances are misleading.

One such method which will serve to illustrate the general approach to the problem is that proposed by Maloney and Schubert (2). This system was developed by application of theoretical analysis of extraction mechanism by Randall and Longtin. The procedure is to determine, by single-stage, batch experiments, tie line data, *i.e.*, equilibrium compositions, sufficient to set up a plot similar to that shown in Figure 4.

Next a diagram like that shown in Figure 5 is drawn with lines for raffinate and extract phase compositions against the weight ratio of solvent and solute present in each phase, selecting the desired composition of extract and raffinate products, by points on the appropriate lines. The operating point D is located by a material balance.

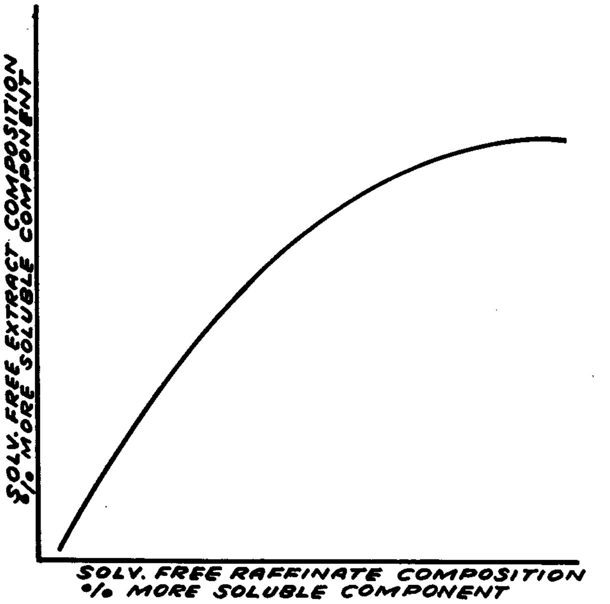

FIG. 4

From the point B locate by the tie line the point A and draw AD, locating E on the extract line. This process is repeated until the feed composition F is reached. Now locate M by drawing DF until it intersects the line representing the raffinate composition and repeat the procedure for the raffinate section of the system.

In using such a method of calculation on a multicomponent feed stock, a convenient physical property may be substituted for solvent-free solute compositions with good results. Before placing a great deal of confidence in calculations for such systems, it is well to check some results experimentally because a very serious error can occur if certain assumptions implicit in the method are not valid. It is assumed that the feed acts like a two-component mixture. Second, it is assumed that although an infinite number of compositions may result in the same value for the physical property chosen to represent composition, all of these which may occur will be identical in all characteristics affecting the performance of the system.

Recourse can be made to pilot plants which are constructed to simulate the results of large-scale units. When this is done, one never knows how many stages are required or how many are realized. Tower design is based on experience to produce a tower which will work as well as the pilot plant. If such experience is not available, the engineer is not helped by the pilot plant data.

Another possibility is to operate a pilot plant made up of actual mixer-settler stages, but such units are usually hopelessly complicated when consisting of more than three stages. Compromises such as the so-called candy-box units often do not operate at high-stage efficiency and are therefore unreliable. Countercurrent batch extractions are probably the best approximations, provided the physical conditions are convenient for such experiments.

The difficulty in correlating pilot plant performance with full scale design is in the great difference between the HEPS (height equivalent to a perfect stage). A 4-in. pilot plant extraction tower cannot be operated so as to achieve the same physical conditions encountered in full scale equipment.

Suppose, for example, a pilot plant is to be used for a propane extraction experiment. It is found that the phase properties are such that a velocity of 100 ft./hr. is selected. The pilot plant is 4-in. ID, and the full scale plant will be 6-ft. ID. The Reynolds number for the pilot plant will be about 5, *i.e.*, below the turbulent flow criterion, while the full scale unit Reynolds number will be 70-80, well up into the turbulent region. Similarly L/D for the pilot plant might be 120 while for the full scale plant 10-15 will be a likely value. Distribution will be no problem in the pilot plant but could become serious in the full-scale tower. In general, the HEPS in the pilot plant might be 2 to 5 feet while in the full-scale tower a factor of 10-20 feet would probably represent a likely factor.

Towers are generally vertical steel cylinders with some sort of internals to prevent by-passing and to promote contacting and separation of phases. These range from slat-baffles to complicated contacting trays and packings similar to those used in distillation towers. Some of these are shown in Figures 6, 7, and 8: 1. baffles—plain, serrated edge, subway grating, and expanded metal; 2. trays—phenol trays. Design of trays is more difficult than for distillation because of high viscosity, low interfacial tension, high drag effects, and small gravity differences.

For most systems baffles of the proper design are satisfactory. Packing has not generally turned out to

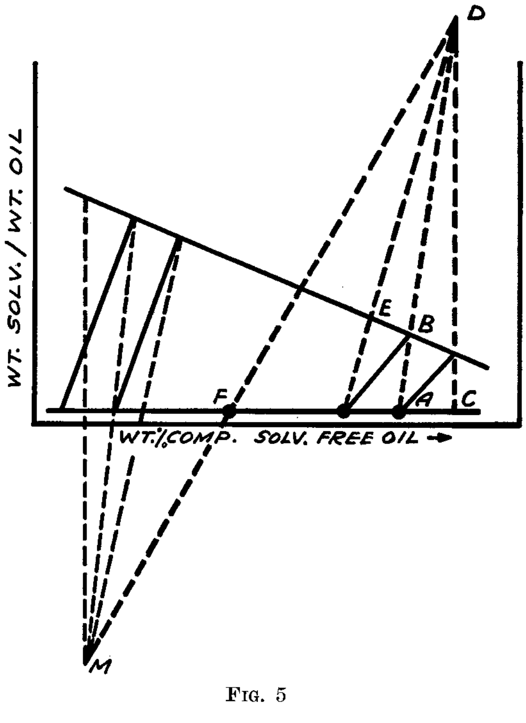

FIG. 5

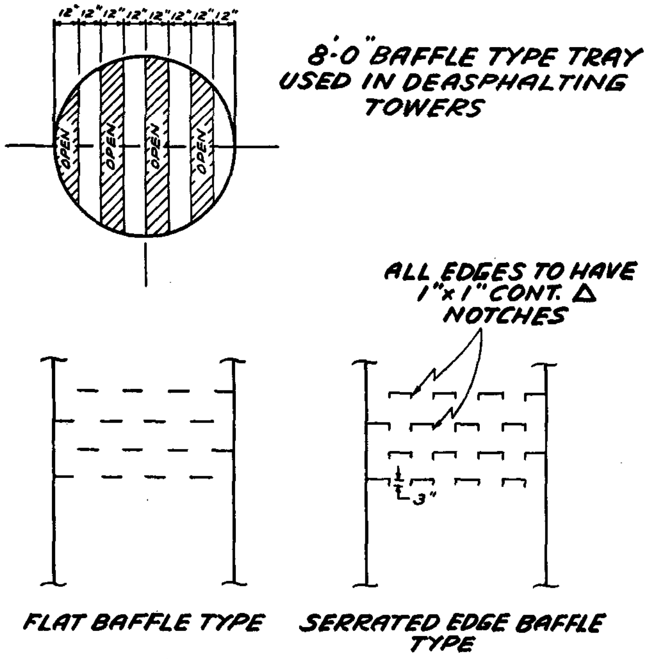

FIG. 6

be better than baffles and is objectionable because of weight, cost, fouling, and breakage.

How to get the required number of theoretical stages in the large-scale tower is a question to which no satisfactory answer can be given. A survey of commercial extraction equipment by Morello and Poffenberger (3) is an interesting reference work which shows that most towers are rated at 3-7 stages. Kellogg has carefully compared countercurrent stage extractions with commercial towers for phenol extraction of lube oils and has concluded that our towers are in the upper end of this range. Internals in these towers are of the tray type, as was shown in Figures 7 and 8.

In general, the purpose of the internals is: 1. to prevent by-passing—and this might be the most important function; 2. to provide mixing or dispersion; and 3. to promote separation of phases (prevent entrainment). By-passing must be prevented at all costs. One phase of the system will almost always tend to wet the walls of the tower and run up or down, by-passing the bulk of the other phase. Mixing is required so that sufficiently large interfacial area will be available for mass transfer. Separation is necessary so that the two phases can continue in the proper direction rather than have the one carried along with the other, thus defeating the purpose of the contacting. Furthermore the dispersed phase should be settled and redispersed as often as possible. Licht and Conway (4) have shown that a very high rate of transfer occurs at the formation and coalescing of the droplets, the rate being relatively slow during the life of a particular droplet.

Mixing should be just sufficient for dispersion. Excess mixing energy leads to turbulence and entrainment, which interfere generally with the performance of the tower.

Settling rates should be high, but it should be remembered that transfer rates are low for large molecules. Thus in such systems too rapid settling causes the dispersed phase to leave the extraction zone before extraction can take place. This occurred in a tallow decolorizing (propane) plant, and it was necessary to raise the level of color bodies well above the propane inlet to permit greater stripping of the raffinate phase before it left the tower.

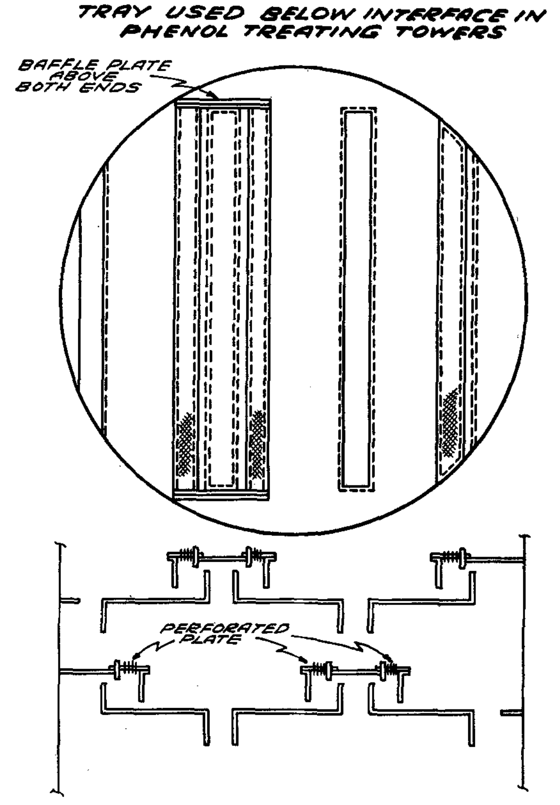

FIG. 7

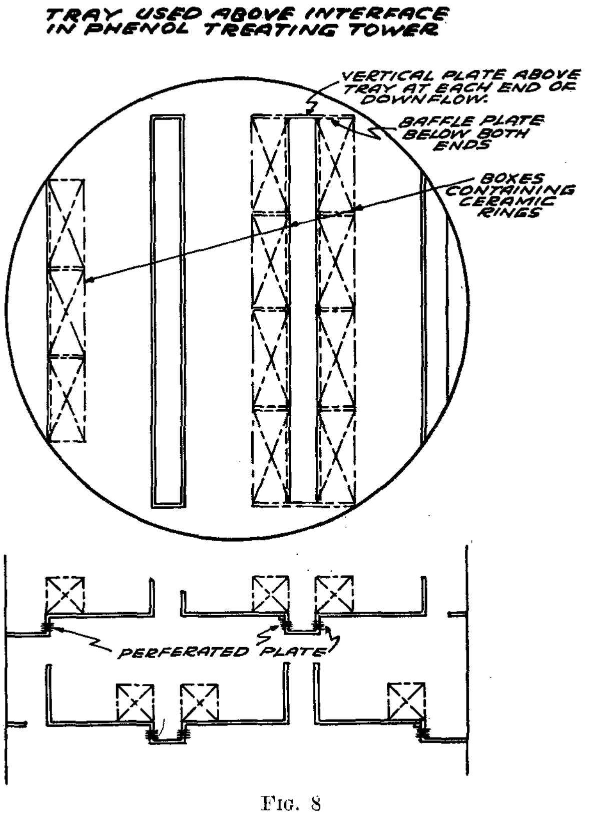

FIG. 8

Tower diameter is of course set by the limiting velocity of the continuous phase. Velocity is limited by the density difference, the viscosity of the continuous phase, and the interfacial tension. The latter is a factor because it determines the drop size obtained under a given set of conditions. Other things being equal therefore the high viscosity phase should be dispersed for greatest capacity.

Another factor which determines the phase to be dispersed is transfer rate. Maximum interface is obtained by dispersing the larger phase, maximum diffusion to the interface is obtained by dispersing the phase containing the largest molecules. The one factor not available for calculating is the film resistance, which in the end may be controlling. Experiments are generally required to determine the phase to be dispersed.

Solvent Recovery

Discussion up to this point has been limited to the extraction system. While this is the most important part of the system from the standpoint of getting the separating job done, it is generally a very minor part of the cost of the plant and is little or no part of the operating cost. The separation of product from solvent and the recovery of the solvent are almost always the major part of investment and operating cost.

Solvent is almost always separated from products by distillation. The recovery system is the place where the energy is put into the process. The operating cost of the recovery system is determined by the reversibility of the energy required, *i.e.*, the extent to which heat can be recovered from hot streams by exchange with cold streams. This is in turn dependent upon the temperatures which can be tolerated by the materials being handled, their boiling points, and the pressures which can be applied.

Recovery of heat, while reducing operating utilities, increases investment. Exchanger surface is expensive. Complicated heat recovery systems generally detract from operability and flexibility. Obviously the nearer the heat recovery approaches the ideal, the more precise the control of streams must be to stay in balance. Furthermore the unit must be capable of starting, not just running.

If the solvent is very volatile, like propane, the availability of exhaust steam should be considered. Usually if steam is available, the exhaust from pumps and compressors in the unit can be used to evaporate most of the solvent. Some high pressure steam is used in a secondary evaporator to evaporate most of the remainder. If one of the products is relatively heat-stable or not of value, a furnace can be used to supply heat for flashing solvent. The cost of solvent and desired product purity are the important considerations in the design of final stripping systems. Usually steam stripping at atmospheric pressure is sufficient for product stripping. The extent of steam stripping depends on the amount of solvent which can be left in the product.

If the product is a vegetable oil for edible use, it will probably be deodorized in subsequent processing so that the traces of solvent will not affect the product purity. Inedible fat destined for soap or paint may contain traces of propane or furfural without harm. On the other hand, propane is dangerous in storage, and both propane and furfural are expensive. It is generally expedient to strip to 0.01% or lower.

It is usually economical to limit the amount of solvent going to the strippers to the minimum permitted by thermal effects in the evaporator because solvent recovered in the stripper must be separated from steam by irreversible cooling and must be handled by the compressor, a very expensive unit.

All irreversible heat must be removed by a coolant, generally water. It should be remembered that the solvent system is closed as regards material and energy, therefore all heat put in by steam or furnace must be removed by a coolant. Similarly the products probably leave at the same or lower temperature than the entering temperature, and if high temperatures are used, these must be cooled. Cooling expense is therefore second only to heating.

Three types of recovery systems are shown: phenol, furfural, and propane.

In illustrating in detail the several solvent recovery systems, there is no intention to make comparisons. The systems chosen and data given are not from the same size units, nor are the extraction jobs the same. The best recovery systems for these different types of recovery problems are represented.

Propane is a low boiling (NBP—40°F.) solvent widely used in deasphalting and dewaxing petroleum oils. It is recovered (Figure 9) by evaporation in steam-heated kettles under sufficient pressure for the use of water-cooled condensers. The last traces left in liquid phase by the evaporators are removed by steam stripping. The recovery of heat is negligible, but the low temperature level permits the use of exhaust steam for most of the heating load. On the other hand, the low temperature level adversely affects the condenser, which is large because none of the heat is removed by exchange. Thus propane condensers are relatively large, and cooling water needs are relatively large.

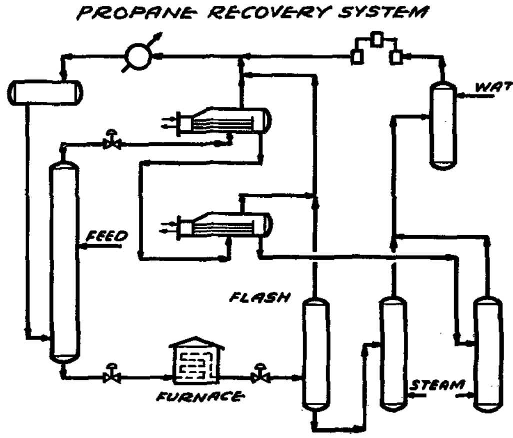

Fig. 9

A heat balance around this system gives a basis for evaluation.

The theoretical duty, *i.e.*, the heat required to evaporate all of the solvent at storage pressure and to raise the temperature of the oil from the tower outlet temperature to the product discharge temperature is 20,000,000 b.t.u./hr. However evaporation, sensible heat of liquid, vapor superheating, steam stripping, and heat of compression make the real duty 42,000,000 b.t.u./hr. The 29,000,000 b.t.u./hr. are supplied by exhaust steam, 300,000 b.t.u./hr. by high pressure steam to the second evaporator. Then 1,400,000 b.t.u./hr. are represented by the heating value of stripping steam, and 300,000 b.t.u./hr. are the mechanical equivalent of the compressor power requirement. Other steam heating, including steam for tower temperature gradient, is 5,000,000 b.t.u./hr., and the asphalt furnace fuel requirement is 6,000,000 b.t.u./hr.

Of this heat input 37,000,000 b.t.u./hr. are removed in the propane condenser, 5,000,000 b.t.u./hr. by other water coolers. There is no heat recovered, but 69% of the total is supplied by exhaust steam. The ratio of heat input to theoretical is 42/20 = 2.1.

The alternate system, in which a multiple effect evaporation scheme would reduce the heat input, has been studied and found uneconomical. Two possible approaches have been evaluated. The first, in which the pressure in the second stage is higher than the first, requires a pump for the liquid. The propane must condense at a temperature not higher than 205° F. (critical is 207°F.) and then further cooled before reduction to storage pressure. This results in a low mean temperature difference, and of course the latent heat is small compared to the sensible heat resulting in a very low transfer rate and very large surface. It has been found that the savings, which are small because more high pressure steam is used, will not usually pay for the additional investment.

A second scheme, in which hot vapors are used to evaporate some of the propane at reduced pressure, results in good latent heat values, higher MTD, and smaller surfaces, but the low pressure vapors have to be compressed before condensation. Up to now the cost of compression has been prohibitive, but it is possible that development of centrifugal compressors may change the picture somewhat.

Furfural is a high boiling (323°F.) solvent used in the refining of lubricating oils, in up-grading furnace oils and cracker charge oils, and for separating glycerides into saturated and unsaturated fractions. The high temperature level makes the heat-economy of recovering this type of solvent somewhat better than for propane.

Figure 10 illustrates a recovery system used in a lube oil refining process. The two-stage evaporation permits the recovery of a large amount of heat by exchanging high pressure vapor against incoming liquid to provide heat for a low pressure evaporation.

The system is somewhat complicated by the formation of a furfural-water azeotrope containing 30-35% wt. of furfural, having a normal boiling point of about 208°F. Fortunately the azeotropic mixture (CBM) separates into two liquid phases, one richer than the azeotrope, the other leaner than the azeotrope. It is therefore possible to collect CBM, distill the two phases in two different towers (A and B), to recover dry furfural as bottoms of one and furfural free water as bottoms from the other, taking the azeotrope overhead from both back to the CBM accumulator.

This recycling of CBM, which is largely water, consumes a considerable amount of heat. Some of the heat, that required to run the A fractionator, is obtained by direct exchange from hot furfural vapors.

A heat balance around a typical furfural extraction unit reveals that the theoretical duty was 27,900,000 b.t.u./hr. Actual gross duty involved was 41,800,000 b.t.u./hr., 153% of theoretical, and the input required was 20,400,000 or 73% of theoretical. Cooling duty was of course equal to heat input, 20,400,000. Compared to the propane recovery system, the heat efficiency of this system is very high, nearly 50% of the gross heating load being recovered. However it should be remembered that only 31% of the propane recovery duty represented a direct load on the power supply, *i.e.,* high pressure steam or fuel.

A third system used for recovery of phenol (Figure 11) is similar to the furfural system but with important exceptions. Water is circulated to the extraction tower, and the phenol-water azeotrope contains only about 8% phenol.

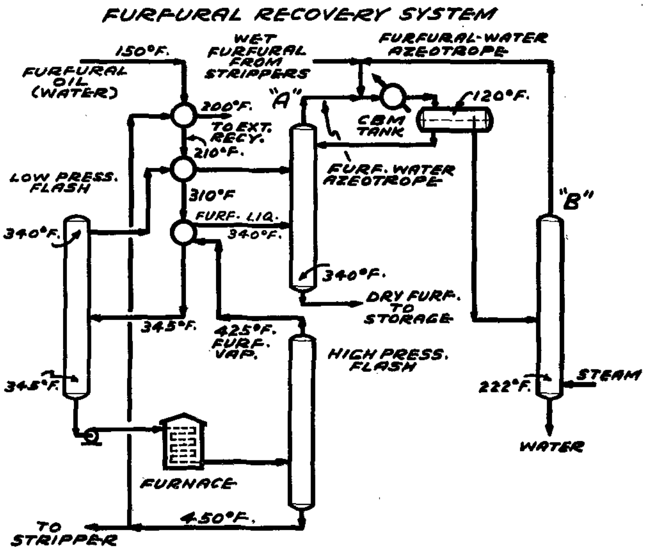

FIG. 10

Again a two-stage evaporation system is used. Furnace heat is used to evaporate phenol at high pressure; the phenol vapors are used to supply heat for the low-pressure evaporation. In the low-pressure evaporation water is taken overhead with 10-15% of phenol. Phenol vapors are taken from a point near the tower bottom and are used to supply heat for preheating the tower feed. Part of the phenolic water overhead is condensed for return to the extraction system, and the remainder is passed through an absorber tower, where phenol is scrubbed out by the incoming oil charge to the unit.

The heat balance shows a theoretical duty of 26,500,000 b.t.u./hr., a gross requirement of 36,500,000 b.t.u./hr., 137% of theoretical, and a net input of 14,900,000 b.t.u./hr., or 55% of the theoretical. Of the gross requirement only 41% is supplied.

The figures given are not meant as a comparison of extraction process economies. The several examples do not represent comparable extraction problems on comparable raw materials. The point to be made is that the economies of an extraction process are set by the solvent recovery problem. The engineering is moderately complex and the systems expensive. Properties of the solvent having nothing to do with its efficiency as an extraction agent can have a profound effect on the recovery cost.

The amount of money to be spent for heat recovery is an extremely complex problem. In the example given for phenol extraction, approximately 22 million b.t.u./hr. were recovered. At a cost of 25c per million b.t.u. (fuel) this amount of heat would cost $132/day, or $48,000/year. Cooling water to remove the 22 million b.t.u./hr. would amount to 1,760 g.p.m. At 2c per 1,000 gal. the cost of water would be $51/day, or $18,500/year. The total saving in fuel and cooling water is then $66,500/year. The cost of installation is not substantially more than for a simpler, less efficient system with a larger furnace and condenser, with the phenol flash operating at substantially atmospheric pressure. Therefore, although the actual heat saved is not quite the 22 million b.t.u./hr. because of the lower flash temperature which could be used if recovery were not made, it is obvious that the savings are large.

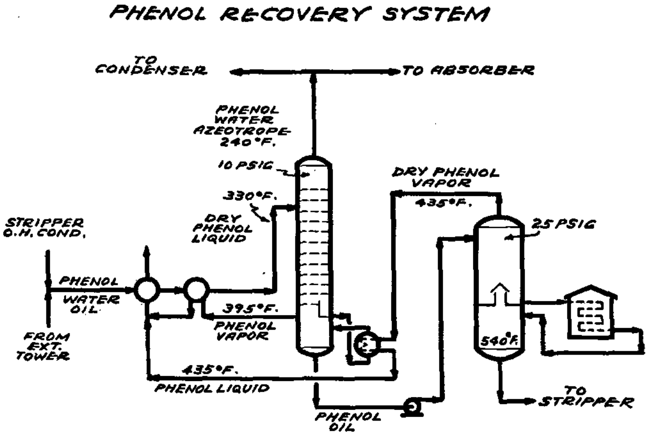

Fig. 11

When the product is heat-sensitive, such as vegetable oils, vitamins, etc., the high boiling solvents must be recovered in more complex, generally more expensive, and less efficient recovery systems. Vacuum strippers and expensive evacuation equipment are usually required. Low boiling solvents, such as propane, are not such a problem. Solvent removal is effected at temperatures of 250°F. or lower.

Complications arising from the use of a second solvent, other than water for which provision must almost always be made, are generally costly, and operability usually suffers.

Materials of construction vary with processes and most of all with materials being processed. Corrosive solvents are seldom used, but some solvents decompose or oxidize or otherwise change to form corrosive compounds. Feed stocks are usually the source of corrosion. Naphthenic acids and sulfur in petroleum, fatty acids in glycerides and tall oils are among the worst offenders. Sometimes although the corrosive components of the feed are in extremely small concentrations, they are volatile and tend to accumulate in the solvent stream, giving rise to corrosion problems far out of proportion to the amounts present in charge stocks.

Protection against corrosion is somewhat outside the field of the process engineer. It is however necessary to specify the nature of the corrosive compounds and those points in the system where they will be concentrated. For example, in the extraction of tallow with propane, fatty acids are present wherever feed or products are present, but the acids might volatilize to a minute extent in the strippers, and the propane compressor must be protected against them because of possible condensation of the acids in the cylinders and discharge ports.

Wherever feasible, corrosive materials are removed by scrubbing, *e.g.*, with caustic, to protect the equipment. When fatty acids are a major component or when caustic would harm the stock, corrosive resistant alloy steels are used. Alloy clad steels are used for large vessels where these represent substantial savings over all-alloy construction. Production of acidic sulfur by decomposition of complex sulfur compounds in asphalt solution furnaces requires use of high chrome-nickel alloy tubes; accumulation of H_2S in propane streams is prevented by caustic scrubbing in the liquid phase.

Pumps

Centrifugal pumps are preferred wherever practical because of their relatively small maintenance cost, adaptability to either turbine or motor drive, and continuity of flow which simplifies automatic control problems.

Reciprocating pumps lend themselves well to application requiring very high pump differentials at relatively small flow rates. They are used to advantage in waxy or high viscosity service where positive displacement is required.

Spare pumps are always an undesirable but often necessary expense. Spare pumps should almost always be provided to insure continuity of furnace charge when failure could mean serious damage to the furnace. When possible, one pump should be electrically driven and the other steam-driven. Furthermore a sufficient accumulation of furnace charge stream should be provided so that the furnace can be cooled properly in an emergency shut-down.

Other spare pumps will depend upon economic considerations. In deciding whether or not to invest in a spare pump, the chief consideration is the cost of a shut-down due to failure of the pump. In continuous processes the cost of shutting down and starting up is usually great, and spares are recommended for all services where failure would necessitate shutting down the plant. It is often possible to use one pump as spare for two or more services since it is unlikely that both would fail at the same time. Sometimes it is necessary to provide pump-out service for blowdown drums and sumps, and these pumps which are used infrequently can often be used as spares for continuous services.

Provisions for Handling High Meeting Point and High Viscosity Materials

Materials of high meeting point and high viscosity make for special piping and exchanger problems. All piping for such service must be steam-traced. This is a very expensive and tedious procedure, but it is necessary. All steam-tracing must be adequately trapped to prevent accumulation of water in the tracer lines.

Very high viscosity service, such as asphalt, requires high pressure steam-jacketing.

Water coolers for waxy or viscous materials must be carefully designed to prevent freezing of fluid on cold tube surfaces. Where a great variation in flow is to be expected, series-parallel double pipe cooler systems, with provision for cutting out some of the surface when necessary, are preferred. In many cases where exceptionally low cooling water temperatures are encountered or very high cloud points are to be dealt with, tempered cooling water and/or concurrent flow is recommended.

Instrumentation

The objectives of instrumentation are three fold: to insure smooth operation of the equipment; to eliminate unnecessary labor; and to protect equipment. Instrumentation for solvent extraction plants cannot be generalized to any great extent. Smooth operation requires flow control of all streams entering and leaving the extraction tower. Usually this is accomplished by controlling the pressure drop across an orifice, using pneumatic transmitters to position the discharge valves from centrifugal pumps. In cases where a viscous charge requires a reciprocating pump, the flow meter controls the speed of the pump.

Streams leaving the tower are controlled by suitable devices for maintaining a constant interface level. These are usually ball-float level controllers designed to control the flow of bottoms solution to maintain a constant interface level. Overhead solution is permitted simply to overflow. The tower top is subject to pressure control when the solution is above its normal boiling point, as in propane extraction.

Recovery systems are instrumented to the extent necessary to insure control of product purity. These usually include instruments to indicate or record temperatures and pressures in distillation equipment, temperatures of streams entering and leaving condensers and coolers, liquid levels in process and storage vessels, and important rates of flow. High and low level alarms, consisting of warning lights and howlers, are usually provided on all critical vessels for protection of pumps against loss of suction and prevention of carry-over in vessels where liquid-vapor separations are made.

All important process conditions, such as rates of flow to and from the extraction tower, extraction temperatures, incoming stream temperatures and recovery system temperatures, intermediate flow rates, and product rates should be continuously recorded in the control room. Important operating control point temperatures and pressures should be indicated in the control room.

All equipment which operates at, or may be subjected to pressure is provided with safety valves connected to the blowdown system. Automatic shut-down devices are installed on pumps to avoid damage due to loss of suction or excessive down-stream pressures.

While good instrumentation is essential to the profitable operation of an extraction plant, excessive instrumentation can be a financial and operating burden. Control instruments are expensive and must be maintained in top-notch condition at all times if they are to operate well. A poorly maintained instrument will seriously interfere with production and product quality control. Pressure and temperature indicators are a great help to the operator in locating causes of trouble and in establishing operating procedures. It may be said that there are never too many of these, but automatic control instruments should be installed only where their function is necessary to good operation.

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