Liquid-Liquid Extraction and Solvent Crystallization

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When it becomes necessary to separate the components of a solution, several methods are available. The most common are distillation, *liquid-liquid extraction, and fractional* crystallization. To these may be added liquid phase thermal diffusion and adsorption, which may eventually become commercially important. Generally extraction and crystallization are considered only when distillation is not applicable: for example, when the components have too small a volatility ratio or form an azeotrope, and when the boiling point at reasonable pressures is so high that thermal decomposition occurs. Extraction or crystallization is also used to separate complex mixtures according to type rather than volatility. For example, a mixture of paraffin and aromatic hydrocarbons containing all possible homologs of each type in a 100°F.-boiling range may be separated into a paraffinic raffinate and an aromatic extract product, by extraction with one of several solvents with a preference for aromatics.

Similarly crystallization can be used to separate meta from para xylene, which boil within 0.6°F. of each other, or stearic from oleic acids, which have similar boiling points and which boil at temperatures high enough to cause substantial polymerization losses. Crystallization is also used to separate wide-boiling complex mixtures according to freezing point, without regard to boiling point, as in the dewaxing of lubricating oils.

Some fundamental considerations in liquid-liquid extraction process design were discussed at the 1953 Short Course, and it is not intended to repeat this material. Attention is called however to discussion of certain methods of using generalized theory to predict or calculate the performance of liquid-liquid extraction systems and to evaluate the requirements of extraction equipment for making satisfactory separations.

Design of extraction equipment has until recently followed more or less conventional lines. Early extractors were of the single-stage type, consisting of a mixer, in which a solvent and the feed mixture were agitated under conditions resulting in the formation of two liquid phases, the phases were permitted to separate by gravity, and finally the settled phases were decanted. Later more stages were added, and a countercurrent flow of solutions from stage to stage was introduced. Finally the countercurrent extraction tower evolved, with internal baffles, or trays, effecting numerous contacts between the ascending and descending phases. All of these designs had a common limitation, the force of gravity. When mechanical mixers were used, the agitation had to be limited so that the dispersion produced would separate by gravity at a rate consistent with a reasonable size of settling zone. In the countercurrent tower, mixing energy is supplied by the force of gravity, and internals must be designed to create a nice balance between the turbulence to provide mixing and the settling rates of the solutions.

Recently there have been introduced commercially applicable designs of countercurrent extractors which tend to overcome some of the deficiencies of the conventional extractors. The R.D.C. or Rotating Disc Contactor consists of a vertical cylinder with horizontal discs on a vertical central shaft. The discs are spaced so as to alternate with "donut" baffles fixed to the wall of the column but not overlapping the discs. The discs are rotated at low speed by an external drive. By avoiding high turbulence but by providing a large area of surface and rotary motion of phases relative to each other, the transfer of components between the phases is accomplished without interfering with settling rates. The over-all effect is considerably to shorten the length of tower required to achieve the equivalent of a given number of theoretical stages, and since there is relatively slight interference with settling, the required diameters are somewhat reduced.

A second, more radical departure from conventional design is the centrifugal contactor. Foremost in commercial development of this apparatus is the Podbielniak model. Briefly this machine consists of a cylinder rotating on a horizontal shaft. Solutions flow countercurrently outward from and inward toward the shaft. Liquids enter and leave through concentric passageways through the shaft and are directed to and from their proper points of entry and egress from the extraction zone by radial pipes or passageways. The flowing fluids are prevented from mixing by mechanical seals. The contacting of phases is effected by concentric, perforated baffles, the design of which is fitted to the properties of the fluids. The passage of the solutions through the perforations produces an extremely high degree of dispersion, which permits a very fast approach to equilibrium. The centrifugal force generated by rotation of the drum prevents entrainment of the dispersed phase by multiplying the gravitational force several thousand-fold. This principle provides a large number of extraction stages and high capacity in a very small apparatus.

Kellogg has tested one of the Podbielniak extractors with a 250-gallon/minute capacity in a refinery in a lubricating oil extraction plant. The extractor was installed to compete with a conventional type of tower of the most advanced design in a plant designed to produce oils of the highest quality. Tests were performed by switching from tower to extractor without change of charge stock or solvent so that there could be no question of the comparability of the results. Several such tests were run on both distillate stocks and heavy residuals. The results of these tests showed that the contactor was at least equivalent to the tower in this service.

Laboratory tests conducted on stocks from several refineries showed the Podbielniak extractor to be a more efficient extractor than most of the towers in operation, and equivalent to the best towers.

Other applications of the Podbielniak extractor seem to confirm our findings. Successful applications include extraction of antibiotics from broth, degumming soybean oil, the separating of phenols from coke oven waste, the refining of sugar cane wax, and continuous saponification, in addition to extraction of petroleum fractions with such solvents as phenol and furfural. The machines are designed so that solids are discharged continuously and do not constitute a fouling hazard. The chief advantages of the extractors are their low hold-up capacity ratio, their small size, and high-stage equivalent.

The success of these new extraction devices, their apparent high efficiency, and their ability to adapt to so wide a variety of extraction problems are most encouraging. It seems reasonable to expect that continued development of extraction apparatus will eventually result in the disappearance of the conventional stages and towers from extraction plant design.

SOLVENT CRYSTALLIZATION for the separation of such materials as fatty oils or petroleum, as distinguished from the separation of normally solid salts from solution, usually require the addition of a suitable solvent for the low-melting components, chilling the solution to produce a solid phase, filtration to separate the phases, and finally recovery of the solvent from both phases as in extraction.

The function of the solvent is multifold. First, the solvent must be selective enough to make the required distinction between the "oil" and the "wax" or "stearin" components. Second, the solvent-oil solution must have low enough viscosity at the crystallization temperature to pass easily through the filter. Third, the solvent dilutes the oil in the liquid phase so that the liquid phase held in the cake contains a relatively small amount of oil. The amount of cake contamination is easily further reduced by washing with oil-free solvent.

Chilling of the charge solution can either be indirect or by auto-chilling, using solvent as refrigerant. Both methods have advantages and disadvantages. If the chilling is indirect, a circulating refrigerant, such as brine, liquid propane, or other suitable material, removes heat from the solution by exchange in double-pipe units, the inner surface of which must be continuously scraped by rotating blades to prevent accumulation of solids on the cold surface. These units are expensive and subject to considerable maintenance and down-time due to wear of moving parts and plugging with solids. On the other hand, control of the chilling is good and movement of solution is continuous, which facilitates uniformity of operation.

Auto-chilling is possible when the solvent has a boiling point below the crystallizing temperature. Sub-atmospheric pressure can be used to extend this range somewhat, but at great cost in chilling horsepower. In an auto-chilling system, using a solvent such as propane, the solution is charged to a suitable vessel and the solvent is allowed to evaporate as pressure is lowered by the solvent compressor until the desired temperature is achieved. Fresh, cold solvent is continuously added to the chiller to replace that which is evaporated. After chilling, the batch is charged to the filtering system.

There are numerous advantages for auto-chilling. There is no separate refrigerant circulating system. There are no cold surfaces to accumulate solids, therefore no scraped surface equipment is needed. The chilling cycle pattern is completely flexible as to rate and solvent/oil ratio. Advantage can be taken of the changing pressure of the evaporating solvent by using compressors with variable compression ratio to reduce installed horse-power. The chief disadvantages are the high pressure equipment required for handling the low boiling solvent, and the batchwise chilling.

FILTRATION is generally carried out in rotary-drum continuous filters. Presses, once widely used, have largely been replaced because they are not suitable for volatile solvents and because of high labor costs and down-time for dumping and cleaning. Pressure differential is maintained by introducing gas to the shell side of the filters and maintaining lower pressure in the filtrate receiver. In this respect auto-chilling systems have an additional advantage in that solvent vapor can be used as shell gas and as blow gas to loosen the cake whereas other systems require a separate gas for this service. Blow gas must be chemically inert to the system; air is excluded if the system is inflammable.

Cake washing is usually required if cake purity or filtrate yield is important. The cake is usually washed with four to six times its volume of cold solvent to displace liquor retained by the porous cake. When cake purity is important, the ratio of solvent/oil in the chilling step controls the ultimate purity attainable. Too low a ratio permits the formation of a high oil content crystal which cannot be improved by washing, but, having produced good crystals, sufficient wash must be provided completely to clear the cake of mother liquor. In rotary-drum filtering proper washing requires low speeds to give time for washing before discharge, and also time to clear internal lines of filtrate and wash liquor lest these be blown back by the blow gas used to loosen the cake. Furthermore, where slurries of high solids content are being filtered, control of filtering rate is required so that the cake build-up is not greater than that which can be washed.

When sufficient solvent and wash are provided, waxes and stearic acids containing as little as about 3% of oil or oleic acid can be produced in one crystallization. Greater purities require a second crystallization, by which means waxes of 0.2% oil have been made.

Multi-stage crystallization for the type of material of interest in this paper has not been developed on a commercial scale although laboratory experiments indicate that extremely sharp separations of complex mixtures can be made. Generally the energy consumption of such systems is extremely high.

As the demand for products with special properties continues to increase, we may look to increased activity in the field of liquid-liquid extraction and crystallization. This increasing activity will undoubtedly lead to the conception of new techniques and new apparatus which will greatly broaden the scope of these separation tools.