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Historical Development

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Introduction

Distillation is one of the oldest and most widely studied unit operations in chemical engineering. It is familiar as a separation technique to chemical, process and petroleum engineers and to chemists. The common techniques, design methods and numerous applications have been extensively documented in monographs and in the journal literature (and conference proceedings) over many decades. Specialist texts and more general handbooks should be familiar to those working in related fields, therefore these standard sources are not documented here. The importance of distillation and its future directions have been discussed by Kunesh *et al*. (1995) and by Porter (1995) (see Further Reading). This article presents a state-of-the-art overview of distillation by concentrating on recent advances and possible future developments.

Sources of Information and Data

For a subject as old as distillation, and with such a wide range of applications, there is an extensive collection of published information. With the advent of electronic databases and online web-based resources it has become much easier to perform literature searches on particular topics and to keep abreast of the current literature and recent developments. For this reason an extensive reference list to journal articles is not provided in the Further Reading at the end of this article. Selected papers are included that can be used to locate related references. Author or subject searches of the journal literature (from 1956 to the present, with six-monthly updates) can easily be performed by using the **CHERUB**^{TM} *Chemical Engineering Database* (complied by M. S. Ray) which is included on the *Engineering & Applied Science CD-Rom Database*. The ability to easily search the chemical engineering literature is a recent development, and is an important advantage for distillation researchers. Another useful reference source is a series of annual update bibliographic papers on 'Equilibrium-staged Separations' (e.g. *Separation Science and Technology* 32(18): 3067–3083, 1997). Patent searches can also be performed on the web, e.g. *www.ibm.com/patents*, and *www.uspto.gov* (the website of the US Patent & Trademark Office). Several handbooks and monographs (and CD-ROMs) containing property data useful for distillation systems have also been compiled, e.g. C. L. Yaws (transport properties data and thermodynamic diagrams); J. Gmehling and co-workers (including VLE data, heats of mixing, azeotropic data); and the *American Institute of Chemical Engineers*' Design Institute for Physical Property Data (*DIPPR*) publications.

Prediction of Vapour–Liquid Equilibria (VLE) Data

Significant advances in the interpretation and prediction of vapour–liquid equilibria (VLE) data have been made since the 1970s. These advances developed from the publication of a range of equations of state (EOS) based upon the application of traditional thermodynamic principles and relationships. The EOSs provide interpretation or evaluation of available experimental VLE data. The Wilson model (1964) is probably the most popular for dealing with liquid-phase activity coefficients because it has only two adjustable parameters, and it works well for both binary and multicomponent systems. The prediction of nonidealities in binary mixtures using the UNIQUAC model (1975) is rather more complex. Subsequent and related studies led to the development and use of the Group Contribution Methods such as ASOG and UNIFAC for the prediction of VLE data. The latter is widely used when actual system data are not available, provided that an approximate nonideality correction is acceptable. New methods are being developed and probably the one showing most promise and of general applicability is known as: A Generalized Approach to Phase Equilibria (AGAPE, 1995).

There are many EOS models described in the literature but only a few have wide use for engineering

applications. The Redlich–Kwong equation (1949) and its modification by Soave (1972), and the Peng–Robinson equations (1976) have broad general application for nonpolar components and are the most widely used, especially in the refining and gas processing industries. For highly nonideal components, use of the EOS requires an appropriate mixing rule. The alternative approach is direct application of liquid activity model parameters in the EOS. A collection of papers relating to the development of the Peng–Robinson EOS over 20 years was published in 1998 (*Industrial and Engineering Chemistry Research* 37(5): 1579–1706).

The availability of commercial software packages, e.g. flowsheeting design packages such as HYSYS™ and PROTISS™ (see below), have made the prediction and evaluation of equilibrium data quicker and easier. These packages were generally developed for use by the oil and gas industry and refining companies, and they include extensive VLE prediction equations integrated within the design methods. Some of these prediction methods have been developed specifically for use with common petroleum systems (e.g. Chao-Seader; Grayson-Streed).

Applications of the Design Methods

Distillation design methods are well established and described in detail in the traditional reference texts (see Kister, 1992). The original methods were formulated in the 1920s and 1930s such as the McCabe–Thiele (1925) and Ponchon-Savarit (1921, 1922) methods for binary mixtures, and the rigorous multicomponent analogues of the Lewis–Matheson (1932) and Thiele–Geddes (1933) procedures. Use of the latter trial-and-error methods emphasized the need for the incorporation of suitable numerical techniques to ensure that the solution (of number of stages) would actually converge, and also to reduce the time spent performing the calculations. Designers later came to rely on short-cut design methods, e.g. Fenske (1932), Underwood (1945, 1946, 1948), Smith–Brinkley (1960), etc., to provide 'ballpark' results before embarking upon the detailed rigorous calculations. Easier access to mainframe computers in the 1960s, and desktop machines in the late 1970s meant that the time required to perform the numerical calculations was reduced, and developments then centred on design methods which simplified the problem formulation, e.g. matrix manipulation techniques.

The arrival in the 1980s of general flowsheeting design packages such as HYSIM™ and PRO/II™ (replaced by HYSYS™ and PROTISS™ in the 1990s) shifted the design emphasis away from the development of specific design methods to the use of commercially available packages which could provide quick and easy short-cut designs. These developments meant that the designer was liberated from tedious calculation but still required a sound knowledge of distillation principles and the ability to analyse the simulation results in order to avoid serious errors. Many papers have been published in the mid-1990s concerning the limitations of the simulation methods (e.g. *Chemical Engineering Progress* 91(6): 63–75, 1995; *Chemical Engineering Education* 31(1): 46–51, 1997), and the problems that can occur if too great an emphasis is placed upon their use with too little feedback from experienced designers (e.g. *Chemical Engineering Progress* 94(6): 63–77, 1998).

Other design packages are available, the most recent developments being the *Computational Fluid Dynamics* (*CFD*) modelling software. Such packages may be useful for modelling effects within distillation equipment rather than straightforward applications of the equilibrium stage calculations. CFD is discussed later in this article in relation to possible future developments.

Advances in Column Design

The basic equipment used to achieve a separation has not changed significantly within the last half century. A tray (or packed) column is still used to provide contact area between the liquid and vapour phases in order to achieve mass transfer and hence the desired separation. Tray columns are generally preferred (packed columns are used for particular types of separations, or specific situations) and the equipment consists of tall vertical towers with a large percentage of internal free space. Distillation is also characterized by its thermal design requirements and is an energy-intensive process. Advances in column design have tended to focus on improvements in energy usage and/or improved separation efficiencies. Two examples from the literature are the Higee distillation unit and the integral dual column. The Higee high-performance distillation or extraction unit described by Ramshaw (*The Chemical Engineer* (*IChemE*) June: 17–21, 1987) attempted to utilize centrifugal fields to improve the separation efficiency and to reduce the column size. The dual distillation columns (see US Patent no. 4 681 661 (1987) and *The Chemical Engineer* (*IChemE*) December: 21, 1987) consists of two concentric columns (the stripping and rectifying sections) arranged one within the other, the reason being an attempt to better utilize heat effects and also to reduce the column height. Neither of these developments (or numerous others described in the literature) has been widely adopted by industry,

possibly because they do not offer significant cost advantages (or because of the conservative nature of the chemical processing industry).

Column Developments

These have centred mainly on a better understanding of the fluid dynamics within the column and specifically across the trays (the first book on this topic was by Lockett in 1986), and also on improved prediction methods for determining plate and overall column efficiencies. A better knowledge of the interrelation of these two aspects is beginning to emerge from several research groups, e.g. Biddulph and co-workers, and their studies of the relationship between Marangoni surface tension effects and plate efficiencies (*American Institute of Chemical Engineers Journal* 37(8): 1261–1264, 1991). A development since the 1970s is the preference for sieve trays, rather than bubble or valve trays which were prevalent up to that time. The *AIChE Bubble Tray Design Manual* (1958) is still used (with modifications) and quoted, even for the calculation of sieve tray efficiencies for which it was not intended and for which it provides rather poor results. However, this older method has provided a starting point for recent studies which examine the significance of fluid-related variables (such as surface tension) and how this knowledge can be used to design more efficient tray columns.

Many papers have been published in the more industry-orientated journals (e.g. *Chemical Engineering* (*NY*), *Chemical Engineering Progress* and *Hydrocarbon Processing*) concerning column operation and performance problems. These papers also discuss particular aspects of internal column design and use of the newer structured packings, now available as alternatives to tray systems, in relation to column performance and operation. The use of high efficiency packings requires a better understanding of the hydrodynamic conditions and the mass transfer processes that occur in the packing. Fouling and plugging within distillation equipment can become serious problems and they are areas in need of better understanding. High surface area packings are popular because they promote efficiency, however they are also more prone to fouling problems.

If solids are present in a stream then design solutions generally act to keep the solids moving. Therefore any liquid maldistribution within the column or tray channelling (due to initial vapour maldistribution) must be corrected to avoid plugging problems. Plugging and fouling have varying effects depending upon the actual in-service conditions, and hence it is difficult to devise generic strategies or solutions. General advice tends to focus upon the need for good distributor design, good wetting (and wettability) of the mass transfer surface, and good distribution of the flow streams within the equipment.

Papers describing column operational problems, such as product draw limitations especially for column revamps (*Chemical Engineering Progress* 94(6), 63–77, 1998), are particularly useful for designers and process operators.

Energy-intensive Nature of Column Design

The energy-intensive nature of column design and operation is unlikely to change significantly, mainly because the requirements for the reboiler to provide vapour flow and the condenser to provide liquid product are essential aspects of the separation. An additional constraint is that the heat removed by the condenser is typically low grade and of little use elsewhere in the plant. Traditional solutions have been to use vacuum operation in the column to lower the boiling point of the mixture (especially for heat-sensitive materials), and to utilize low-grade heat from other plant operations to provide the reboiler duty. Attention has been directed towards lowering the energy requirements of a column, e.g. by reducing the reflux ratio. Energy-saving revamps have replaced trays with packings in order to create more theoretical stages within a column, and hence reduce the reflux rate and boil-up rate. The integration of columns within a sequence and the use of overhead vapours in another column's reboiler (e.g. by use of a Rankine cycle) have also been considered. Energy saving and integration techniques have become standard design procedures since the 1970s (including the use of pinch technology and heat exchanger network design). However, it is difficult to achieve (or to envisage) large scale reductions in the thermal requirements of distillation due to the inherent basis of the separation itself, i.e. latent heat of vaporization is required for the essential partial vaporization at each stage. The most likely developments in this area are the use of hybrid systems, e.g. membranes + distillation, which effect a part of the separation in a less energy-intensive operation (see the section below on developments and applications).

Particular Techniques and Situations

This section considers only two specific aspects of distillation operations, namely process control and difficult separations (e.g. azeotropes).

Chemical Process Control

This was mainly in the hands of electrical/instrument engineers until the mid-1960s, and most of the

published literature reflected their particular expertise. Since that time process control has developed as a significant area of chemical engineering expertise and publication. Many academics have adopted and published in this field (see Luyben, 1992) and there are also several handbooks and practical texts dealing with plant operations (e.g. Shinskey, 1984). Distillation was one of the primary chemical engineering unit operations to be researched and developed in depth for process control applications. This was because of the scope offered by distillation as a control problem and the range of options and alternatives available. The focus of distillation control is usually the product specification, but the critical operations of reboiler and condenser performance, the uncertainty of feedpoint location, the reflux rate, and the need for correct internal functioning (e.g. fluid flow on and between the trays) means that several complex relationships and problems need to be considered together. The number of publications dealing specifically with distillation control attests to the complex nature of the problem and the number of approaches and applications that are possible within any single situation. An additional consideration for the designer is the possible number of column arrangements, utilizing several columns, and their possible alternative specifications (hence the advantages offered by simulation packages), and therefore the integration of individual column control within the overall control of a set of distillation operations.

Developments in distillation control have focused on several areas, generally searching for optimal solutions to the following:

1. Individual column control (including reflux streams, and reboiler and condenser operation and performance).
2. Control of a column required to perform a specific separation (e.g. heat-sensitive mixtures) or a particular type of application (e.g. separation of azeotropes or close-boiling mixtures; reactive distillation).
3. Control of sequences and arrangements of several columns.

Distillation control has developed into a multifaceted problem incorporating mass transfer and separations, process modelling and optimization techniques, instrumentation and control functions, and the application of simulation packages in order to evaluate a range of possible problem solutions. Control theory has now developed to include a range of advanced techniques such as adaptive control, model-based control, and the use of neural networks which supplement the basic approaches offered by combinations of proportional, integral and derivative (P-I-D) control functions.

Difficult Separations

Difficult separations using distillation techniques depend primarily upon the nature and properties of the components in the mixture, rather than the physical arrangement of the equipment such as bubble caps versus sieve trays, tray versus packed columns, etc. Reactive distillation is an exception to this generalization (see next section). Distillation contrasts with other separation techniques such as membranes and adsorbents where the characteristics of the actual separation media have a significant effect upon the ability to separate the components. This is why generic distillation methods have been developed and used effectively whereas there is no single theory or method available for the design of either membrane or adsorption systems. However, distillation was developed in order to separate mixtures of components exhibiting significant differences in relative volatilities and boiling points and problems arise where this is not the case. In particular, azeotropes exhibit no difference in volatility (at certain conditions) and hence no change in the composition of the mixture obtained. Traditional approaches have been either to avoid the conditions where an azeotrope forms, or (more likely) the addition of a solvent or entrainer which 'breaks' the azeotrope but which also requires an additional column(s) to remove and recycle the solvent. The common azeotropes are well known and documented, e.g. ethanol/water, acetone/chloroform, etc. Recent developments have centred on the ability to predict the occurrence of an azeotropic mixture (or a mixture with very little difference in component volatilities), and also on the application of the traditional design methods to the design of a range of column configurations. These configurations aim to produce an optimum separation in terms of product specification, minimum use and recycle of solvent, effective and feasible control schemes, minimum capital and operating costs. Computer-based property packages have been developed specifically to predict azeotrope formation, and the vapour–liquid equilibria data can then be used in an appropriate column simulation package to evaluate the alternative equipment arrangements. Researchers have developed prediction and property packages by the application of basic thermodynamic principles, and also utilizing specific equations of state (see section on VLE data above). The property packages have also included data on available solvents. The aim is generally to combine azeotrope prediction with solvent selection, and full specification of the combined mixture properties for use in column design simulations.

Developments and Applications

Reactive or Catalytic Distillation

Reactive or catalytic distillation has emerged as a significant development in recent years, the original patents were obtained by L.A. Smith in the early 1980s. Several research groups have considered a range of specific systems and applications and a substantial body of literature has been published. The main system that has been investigated and reported is the production of methyl *tert*-butyl ether (MTBE) mainly due to the high efficiency of the process, and also the related systems of ethyl *tert*-butyl ether (ETBE) and *tert*-amyl methyl ether (TAME). The technique includes reactive (homogeneous catalyst) or catalytic effects (heterogeneous catalyst acts as the packing) within the traditional distillation equipment. The design requires a combination of the well-known mass and energy balance equations with the individual reaction mechanisms, and consideration of heats of reactions. The design of such systems requires modelling of the mass transfer, reaction and separation, thermal effects, and the inherent control systems. An additional requirement is the knowledge of any possible side reactions and by-product formation, and their effect on the final separation of the mixture produced.

If a catalyst is required then the physical installation of this material, its removal and replacement, and its effect upon the fluid dynamics within the column become important additional operational and design considerations. The distillation column now becomes a countercurrent two-phase flow, fixed-bed reactor. Packed beds typically have a void fraction of 0.7 (even up to 0.95), whereas small catalyst particles result in a voidage of 0.3–0.4 which makes countercurrent operation impractical. Therefore catalyst support structures must be designed and incorporated to provide a voidage of at least 0.5, and in addition allow for expansion and contraction of the bed, and provide a uniform catalyst spatial distribution. An alternative is to manufacture the catalyst in the shape of a distillation packing. For certain systems there are distinct advantages from employing reactive distillation, but their dynamics are complex and careful consideration of the operation and control are required in order to avoid potential difficulties.

Hybrid Separation Systems

Hybrid separation systems combining two or more unit operations have become popular in the 1990s, and there are numerous examples in the journal literature. Many of the examples have combined distillation with a membrane-type technique, thus aiming to utilize the well-known data and methods (and separation efficiency) of distillation with the low temperature advantages offered by membrane systems. Osmotic distillation (or isothermal membrane distillation) has been developed specifically for applications requiring the retention of flavours and fragrances (*Chemical Engineering Progress* 94(7): 49–61, 1998). This hybrid process can concentrate solutes to very high levels at low temperatures and pressures, and it is particularly suitable for sensitive solute materials. It can also effect the selective removal of a single volatile solute from an aqueous solution. The process involves the transfer of volatile components between two inherently miscible liquid streams, separated by a semipermeable membrane, the driving force being provided by differences in component activity between the streams. The strip solution becomes diluted during separation/transfer and must be reconcentrated by distillation (or evaporation). Many other examples of membrane–distillation systems can be found in the literature. Alternative hybrid systems include crystallization–distillation, solvent extraction–distillation, pervaporation–distillation, and fluidized reaction–distillation. These systems have been described in some detail including patents, although generally the work is directed towards a particular application or problem.

The Future: Developments and Applications

Future developments would seem to be most closely linked to the areas already outlined in this chapter rather than sudden and unexpected applications. Distillation is a mature separation technology and developments are likely to be in incremental advances in our knowledge and understanding of the process itself, and in the underlying principles that determine its ultimate effectiveness for separating components.

The most likely areas for significant advances and developments are:

1. Further combinations of mass transfer effects within distillation equipment (tray or packed columns), developing the current trends of reaction with distillation (reactive and/or catalytic distillation), and hybrid systems of membranes (or other techniques) with distillation.
2. Improvements in separation effectiveness (and costs) including attempts to reduce the size of the equipment, increased efficiencies, and reductions in energy requirements.
3. More reliable prediction and modelling techniques directed towards VLE predictions, efficiency models and predictions, and improvements in the CAD

modelling packages in order to identify practical limitations of the simulations at an early stage.
4. Development of separation systems incorporating distillation in order to address specific environmental problems and applications.

Significant applications are expected in the use of *computational fluid dynamics* (*CFD*) *packages* for prediction of effects occurring within distillation equipment. This is a different area of research from the use of the flowsheeting packages and the calculation of equilibrium stages. The CFD approach (generally using commercial packages such as PHOENIX™ and FLUENT™) has been used to predict single-phase flow patterns (of a vapour phase) from numerical solutions of the Navier–Stokes equation, turbulence equations, and the continuity equation. If the equations of momentum and mass transfer are inserted into the CFD methodology then it may be possible to predict the flow patterns and their effects upon tray performance. However, the major challenge is the consideration and modelling of the three-dimensional froth height and its shape.

Reviews of the state-of-the-art in distillation and the need for and possible directions of future research have been discussed by Fair (1988), Kunesh *et al*. (1995) and Porter (1995). Assessments of advances and developments in distillation equipment regularly appear in the journal literature, e.g. *Chemical Engineering* (*NY*), December 1992; *Hydrocarbon Processing*, February 1989; *The Chemical Engineer* (*IChemE*), September 1987. Fouling and plugging in equipment and a better understanding of the internal flow mechanisms and regimes are areas receiving and requiring further attention, as discussed earlier. Most new ideas tend eventually to become either an academic curiosity, or niche applications, and approximately every 10 years a new technique gains attention and prominence, e.g. reactive distillation, membrane–distillation.

See Colour Plate 38.

See also: **II/Distillation:** Energy Management; Instrumentation and Control Systems; Modelling and Simulation; Theory of Distillation.

Further Reading

CHERUB™ – **CH**emical **E**ngineering **R**eference **U**ser **B**ibliography on the *Engineering & Applied Science CD-ROM* from INFORMIT, Melbourne, Victoria, Australia (published semi-annually by subscription; details available from this author).

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Instrumentation and Control Systems

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Introduction

Distillation columns have been widely used in the past to separate mixtures of liquids into individual components. And even though new separation techniques are being developed, distillation remains the most important separation method applied in the process industries today.

The layout of a simple distillation column is shown in **Figure 1**. A single feed enters the column at the side and two products are produced: the light or most volatile components are withdrawn from the top and heavy components are removed from the bottom. Heat (in the case shown, steam) for evaporation of the liquid is supplied to the reboiler, and heat is removed (in this case, through cooling water) at the top in the condenser. The nomenclature used in this