

Separations: A short history and a cloudy crystal ball.

Phil Wankat
Purdue University

Abstract

Separations have played a major role in the history of chemical engineering and will continue to be important. Since separations have always been the major cost item in the process industries, they have always been a critical key to successful commercialization. Many separation processes such as distillation, adsorption, chromatography and filtration were used long before they were understood. First, the history of separation processes will be reviewed. Next, we will discuss the current teaching of separation processes. The final part of the talk will explore predictions for the future of applications, teaching and research funding in separation processes.

Introduction

Separations have always been and will continue to be critically important in the processing of chemicals. It is common to note that 40 to 70 % of both capital and operating costs in industry are due to separations [1, p. 1]. It has been estimated that 15 % of the world's energy use is required by separations [2]. Because of its industrial importance separations have always played an important part in chemical engineering education and in the chemical engineering literature.

History of Separations

The beginning of separations apparently occurred before recorded history. Egyptians used filtration to filter grape juice over 5000 years ago [3, pp. 89-90]. Aristotle mentioned that pure water can be obtained by evaporating sea water [4, p. 16]. A combination of coagulation of impurities, evaporation, and crystallization used for salt manufacture were commonly in use by the 16th century [3, p. 90; 4, pp. 21; 5, pp. 229-233]. Similar practices were still in use in India in 1980 [5, p. 233]. Pressing, evaporation and crystallization were commonly in use for sugar production by the 16th century [4, p. 23].

Distillation, particularly batch distillation, has a long history. Mesopotamian clay distillation vessels with lids shaped to collect the condensed volatile distillate have been dated to ~3500 BCE [6]. Alchemists in the first century AD in Alexandria used a variety of simple batch stills or retorts [4, p. 16]. The alembic still was invented by Jabir ibn Hayyan (aka Geber) in the late 8th or early 9th century. Similar stills are currently in use in some whiskey distilleries and for distilling rose oil [6]. By the 14th century the production of strong alcoholic drinks had become an industry [4, p. 18]. The first books on distillation were Hieronymus Brunschwig's *Liber de arte distillandi*, in the early 1500's and Walter Ryff's *Das New gross Distillier Buch* in 1545 [7]. Petroleum distillation was started in England in the 17th century and coal tar distillation was first patented in 1746 [4, p. 35]. Fractionation of coal tar into naphta, kerosene, lubricating oil and paraffin was patented in England in 1850 [8]. The first oil refinery constructed in 1860 in Pennsylvania used simple batch stills and collected wide-boiling fractions as the distillation proceeded. Horizontal stills with improved performance were used in the early 19th century for alcohol purification. An improved still was developed in 1818 by Cellier in France who developed a vertical bubble plate still for alcohol purification [4, p.35]. In his *Handbook of Chemical Engineering*, published in 1901 and in an enlarged edition in 1904, George Davis clearly developed the unit operations idea (not by this name) for distillation [9, pp. 100-103]. Before this, the distillation of each chemical was studied separately. It is notable that the 2nd edition of C. S. Robinson's, *The Elements of Fractional Distillation*, [10] has elements of both

the unit operation generalization and individual chapters for distillation of a number of chemicals such as ethanol. By the fourth edition, extensively revised by Ed Gilliland [11], the unit operations approach dominated and distillation of specific chemicals were relegated to examples. *The Elements of Fractional Distillation* may have been the first chemical engineering book to also become popular with a non-technical audience – it was very popular with bootleggers in the 1920's and 1930's [12, p. 85]. Batch distillation was important enough to attract the attention of Lord Rayleigh who apparently did the first theoretical analysis of the method [13].

The first continuous distillation appears to have been developed by Aeneas Coffey in 1830 who developed a vertical perforated plate column for alcohol purification [4, pp. 35-36; 13a]. This still was equipped to preheat the feed by exchange with the condensing distillate and the bottoms. In 1900 vertical perforated plate columns quite similar to modern equipment were introduced for distillation of tar [4, p. 36]. Packing was apparently first employed in 1820 and was patented in 1847 [14]. The problem of breaking the ethanol-water azeotrope was solved by Young in 1902 with a batch, azeotropic distillation process using benzene as the entrainer to produce the first observed ternary azeotrope as the distillate product. The batch process was converted to a continuous azeotropic distillation by Keyes in 1928 [15].

In the early 1920's petroleum refineries had not adopted more modern fractionation systems and were using horizontal stills directly heated on the bottom in conjunction with partial condensation to distil petroleum. These systems were not very efficient and considerable redistilling was required. Modernization of distillation in refineries occurred in the 1920's when W. K. Lewis was hired as a consultant by the Standard Oil Company of New Jersey and introduced vertical fractionation systems [8, pp. 305-306]. By the 1920's and 1930's the schematics of continuous distillation columns in textbooks [10; 16; 17] and in Perry's Handbook [18, section 12] look fairly modern except that valve trays and structured packings had not been invented yet. Heat recovery from distillation was common by 1923 [16, p. 575]. The histories of distillation equipment, distillation control, and azeotropic and extractive distillation were reviewed by Fair [14], Buckley [19], and Othmer [15], respectively, for the 75th anniversary of AIChE.

Theoretical analysis of continuous distillation was first achieved by Sorel, who was interested in the distillation of alcohol [20]. Sorel's method is accurate, but confusing and laborious since a trial-and-error calculation was required on every stage. It was analyzed graphically without trial-and-error by Ponchon [21] and Savarit [22] independently. Lewis [23] realized that in many cases the vapor and liquid flow rates are approximately constant – if they are assumed to be constant Sorel's trial-and-error procedure is not required. The simplified Lewis method was converted to a graphical method by McCabe and Thiele [24]. Because McCabe-Thiele plots clarified the physical reasons why column distillation work, the method was rapidly adopted. While no longer used for design, McCabe-Thiele diagrams are commonly used to teach distillation. Solutions for multicomponent distillation are much more complicated, particularly if there are non-distributing light and heavy non-keys. Initially, stage-by-stage methods were adapted to multicomponent distillation [25; 26], but closure remained a problem. Numerous computer solution methods were developed after Amundson and Pontinen [27] realized that distillation equations could be conveniently solved after they were put into matrix form. One of the more robust and common methods still used in commercial simulators was Naphtali and Sandholm's [28] linearization of all the equations. The history of distillation models was reviewed by Holland [29] for AIChE's 75th anniversary.

Unlike distillation, which developed gradually over centuries, practical application of absorption appears to have been developed solely by a single person in 1836 [4, p. 29]. William Gossage used an old windmill as a tower to absorb HCl in a downward flowing stream of water. The

column was packed with gorse and brushwood. This inspiration soon led to towers packed with various materials such as twigs, broken brick, coke and stone to absorb HCl. A next step was the development of high efficiency CO₂ absorption towers by Ernest Solvay for his Solvay process [4, pp. 29-30]. Theoretical analysis of absorption was facilitated by the development of the two-film theory of mass transfer [30].

Crystallization from solution was one of the key tools of the alchemists [31], and remains partly art. In 1878 Gibbs studied the thermodynamics of growing crystal surfaces at equilibrium and realized that thermodynamics was often not sufficient to explain the crystal growth [31]. McCabe [32] found that the deposition rate/unit area is often linear in supersaturation and deposits grow at a uniform rate. Unfortunately, McCabe's ΔL law often does not hold [31]. Industrial scale crystallizers in 1934 [33] did not look very different than many modern crystallizers. The important theory of crystal size distribution was developed by Randolph and Larson [34]. Hulbert [31] reviewed crystallization for the 75th anniversary of AIChE, and more recent advances in crystal engineering are reviewed by Doherty [35].

Membrane filtration developed at least as early as 1600 BC when the Arawak people of the West Indies used porous stone filters to purify drinking water [36]. With this exception, the development of membrane separations is almost unique since the science was developed before practical applications. The first studies of membrane phenomena were done by Abbé Nollet in 1748 who studied permeation through a semipermeable membrane [37, p. 82]. In 1855 Fick studied diffusion and developed the laws of diffusion still used to study membranes [37, p. 82]. Thomas Graham studied dialysis in 1854 [38] but it was not until 1944 that Kolff and Beck developed a commercial dialyzer – the artificial kidney [37, pp. 95-97]. Graham studied gas separations in 1863 [39] but it was not until 1954 that Kolff and Balzer developed a membrane lung oxygenator that was improved by the work of Clowes and coworkers [37, pp. 131-133]. Pauli developed electrodialysis in 1924 [36] and the multicell electrodialyzer was developed in 1940 [37, pp. 98-99; 40], but electrodialysis did not become practical until the 1950s with the development of synthetic ion-exchange membranes [37, p. 100]. The *seminal* development that led to large scale commercial applications of membranes for pressure driven systems was the Loeb-Sourirajan method of producing asymmetric membranes with a defect-free thin skin [37, pp. 104-105; 41]. This method rapidly led to commercial reverse osmosis systems in the 1960's [37, p. 104; 42]. Loeb-Sourirajan membranes could also be used for ultrafiltration (UF) if the membranes were not annealed. This led to commercial UF systems, but they were severely hampered by concentration polarization. The eventual understanding of concentration polarization led to the development of flow regimes and membrane modules that allowed for practical applications of UF in the mid to late 1960s [37, pp. 117-125]. After Monsanto developed the Prism membrane separator for hydrogen purification in 1979 [37, pp. 129-133; 43], several other commercial gas permeation systems were developed [42]. Pervaporation can be traced to the work of Graham, but the definitive studies were done by Binning and his co-workers in the late 1950s and early 1960s [44]. Pervaporation was first commercialized in the 1980's for breaking the ethanol-water azeotrope [42].

Adsorption, particularly the use of charcoal to purify water, has been known since Biblical times [45, Vol. 1, p. 82], and was used commercially in 1794 for the clarification of raw sugar [46, p. 1075]. Scheele studied the adsorption of gases on charcoal in 1773 [47, p. 548], and the ability of charcoal to remove odors from air was extensively studied by Hunter in the 1860s [46, p. 1087]. Clay was also extensively used with an early use in “fulling” (the removal of grease from wool – hence the name fuller's earth) and processing vegetable oils, and later applications in petroleum processing with percolation processes [46, pp. 1059-1061]. Thermal desorption including burning the adsorbates off of the adsorbent was the common regeneration method if the

adsorbent was regenerated. Solvent recovery with activated carbon followed by steam desorption has been commercially practiced since the 1920s with little change in the basic equipment [45, Vol. 1, p. 73]. Pressure swing adsorption (PSA) developed by Skarstrom [48] at Esso in the 1950s and 1960s allowed for much faster cycles and thus higher productivity. PSA was rapidly developed for air drying, hydrogen purification and air separation. Simulated moving beds (SMB) were developed by Broughton and his coworkers at UOP during the same time frame to solve the attrition and mixing problems that occurred in moving beds [49; 50]. This process is similar to the Shanks process (1841) used to simulate counter-current flow in leaching [51, p. 723-724]. Two major commercial applications of the SMB have been purification of p-xylene and separation of fructose and glucose [45, Vol. 2, chapt 6].

Ion exchange can also be traced to biblical times [47, p. 549]. Scientific studies were first done by Thompson in 1850 using naturally occurring clays [52; 53, p. 163]. The first major application of ion exchange, water softening, occurred early in the 20th century [47, p. 549]. The major advance in ion exchange was the development of synthetic polymeric ion exchange resins in England in 1935 [54]. Synthetic polymer resins were used by Frank Spedding and his co-workers for large-scale chromatographic separation of the rare earths in the Manhattan project during and immediately following World War II [54; 55] and are currently used for almost all ion exchange applications including home water softening. Moving bed systems with intermittent or pulsed solids movement have been used for large-scale ion exchange systems, particularly for water treatment, since the 1940s [45, Vol. 2, pp. 68-76]. Applications of ion exchange for biochemical separations followed the demonstration of the power of ion exchange chromatography [56; 53, p. 163].

Liquid chromatography in the form of column elution chromatography was first developed by Tswett in 1903 [57]. He called the method “chromatography” because he observed colored bands moving down the column. Large scale applications of very similar systems were commercialized in the late 1940s for separation of carotene, xanthophyll, and chlorophyll on an activated carbon column using gradient elution and backwash, and in the 1950s the Arosorb process developed by Sun Oil Co. was used to separate aromatics from alkyl hydrocarbons using silica gel [45, Vol 2, p. 1]. Currently, commercial applications of liquid chromatography are common for bioseparations. Liquid-liquid chromatography (LLC) was developed by Martin and Synge [58] and gas-liquid chromatography was developed by James and Martin [59]. Although very successful in analytical applications, neither of these methods has been successful as a large-scale system. However, LLC led to bonded phases that are used commercially in large-scale systems. Scale-up of size exclusion chromatography (SEC) was much more successful, and SEC was used for large-scale separations shortly after it was invented [60].

Teaching Separation Processes

The key questions remain, What to teach? and, How to teach it? [61; 62]. If we had as much time as was needed, we could teach all the separations in a separations oriented ChE curriculum [62]. Because this curriculum is process oriented and uses separations as the unifying theme, it does not fit into current trends in curriculum development [63; 64], but I think industry would like it.

With an overcrowded curriculum separation methods are not going to receive significantly more time; thus, we must choose which separations to include. In my junior level course I have chosen to cover flash distillation, normal and complex continuous distillation (binary, multicomponent, extractive and azeotropic), batch distillation, absorption and stripping, liquid-liquid extraction, and membrane separation. To cover this significant amount of material, extraction is taught at a purely equilibrium level with no design, and membranes are usually limited to gas permeation

(but including all flow patterns). I use my own textbook [65], although there are other good textbooks available [e.g., 47; 66; 67]. Obviously, this choice of material leaves out many important separation processes. Some of these are easily included in senior laboratory (e.g., drying and chromatography) or senior design courses, but the students rarely have the same level of understanding of theory. It is also important, if possible, to have dual-level (graduate and undergraduate) electives available on topics such as particulates [68], rate separations [69], bioseparations [70] or advanced distillation [71].

Since the modern practice of chemical engineering uses process simulators and other computer tools extensively, these tools need to be used in the separation course(s). For distillation and the other equilibrium-staged separations, process simulators are used for design and simulation in industry and thus should be used in undergraduate courses [72; 73]. The particular process simulator used is not critical. Since membrane separators are not simulated in AspenPlus, spreadsheets can be used for membrane systems [65; 74]. Spreadsheets [75], MATLAB and Mathematica [76] are useful for solving problems and helping students understand the equilibrium-staged separation methods. Use of these tools requires that class time must be set aside for their use – preferably in a computer laboratory. Use of these tools also helps graduates satisfy ABET’s criterion 3k, “an ability to use the techniques, skills, and modern engineering tools necessary for engineering practice.” [77] Simulators should also be used in dual level electives [69; 71]. The “lecture” portion of the courses should use well known active learning methods [72; 73; 78] in addition to mini-lectures.

Predictions

Where are the industrial use, education and research funding for separations headed? My crystal ball is cloudy, but I will hazard predictions. These predictions assume that the one great “killer” application that makes a host of existing separation processes obsolete will not appear and that funding for academic research on separations will remain tight despite the identification of a number of high priority research areas in separations [79].

First prediction - Distillation: Distillation will remain the major industrial workhorse and a major, although probably slowly declining, part of education in separations. Education in distillation (including absorption and stripping) will increasingly focus on the use of process simulators. Unfortunately, funding for academic research on distillation will remain anemic in the USA.

Rationale – Industrial Use: Distillation will continue to be the industrial workhorse because: 1. It is trusted. 2. It is understood well enough that existing computer models will produce designs that work in about 80 % of cases [79, p. 25]. 3. Except for extractive and azeotropic distillation, mass separating agents are not required and thus do not need to be recovered. 4. A complete binary separation is possible, which means a component can be recovered with high purity and high recovery. 5. In many cases distillation is the most economical separation process. 6. Currently, 90-95% of all separations in the chemical process industry are done by distillation [1, p. 11].

Rationale – Education: Because of the broadening of positions that graduates accept, most schools want to prepare students for jobs outside the traditional chemical and petroleum industries. Thus, there is considerable pressure to teach other separations, but additional time is rarely allocated to separation processes. Process simulators will be used because they prepare students for industrial practice, they are now readily available at most schools, they are supported by textbooks, ABET encourages the use of modern tools, and they help students learn.

Rationale – Research Funding: The USA funding agencies have to a considerable extent apparently decided that distillation is a known art and that companies or Fractionation Research Inc. (FRI) should conduct any research needed. This reasoning ignores that even small advances in distillation can be economically important, and that a paradigm shift, although perhaps unlikely, would have enormous economic impact.

Second prediction: Mechanical separations such as filtration, centrifugation and settling will continue to be ignored in the ChE core at most schools although they will remain critically important in industry. Funding for research in particulates will remain reasonably secure.

Rationale – Industrial Use: Because unwanted solids must be removed and many products are sold as solids, particulate separations will remain industrially important.

Rationale – Education: Unfortunately, at the time that the engineering science revolution changed chemical engineering education, many steps in handling and processing solids were art not science. These unit operations were often dropped from the curriculum since they were not considered to be scientific. Many schools have added these processes back into the curriculum, but in an elective on particulates instead of in the core. Because of time pressures on the core, mechanical separations are unlikely to be added to the core in a meaningful way.

Rational – Research Funding: The mechanical separations have found a home in the general area of funding for particulates. Although not overly generous, this funding is probably secure.

Third prediction: Membrane separation processes will continue to find industrial applications, but at a slower rate than predicted by researchers. Membrane research will continue to benefit from support that is robust compared to that received by other areas of separation. Membrane separations will become an increasingly common part of separation courses in the ChE core.

Rationale – Industrial Use: In applications where they work well (high selectivity and high flux, commercially available, high purity *or* high recovery but not both is required, minimal fouling occurs and the membrane has a long life) membranes are often the least expensive separation method by far. Unfortunately, fouling, relatively short membrane life, and lack of membranes with suitable selectivity often limit use of membranes even when both high purity and high recovery are not required.

Researchers in all areas are always overly optimistic about applications of their new inventions – this appears to be particularly true of membrane researchers.

Rationale – Education: Since industry is using membrane separations more, there is a desire to cover this material. Membrane separators are now included in many textbooks, and the level of presentation is accessible to undergraduate chemical engineering students.

Rationale – Research Funding: Funding agencies appear to believe the myth of a killer application for membrane separators without realizing their fundamental limitations. Thus, membrane separators are the only separation systems that are funded at close to a reasonable level. Since myths seem to live forever, this rate of funding will probably continue.

Fourth prediction: Adsorption, ion exchange and chromatographic separation processes will slowly become more important in industry and will continue to receive modest research support, particularly for biological applications. These processes will be taught mainly at the graduate

level. Their lack of coverage at the undergraduate level will continue to serve as a barrier to their wider application in industry. Research funding will remain tight although it will be somewhat more available for biological applications.

Rationale – Industrial Use: Adsorption, ion exchange and chromatographic separation processes can often accomplish separations more economically than other methods. This is particularly true in biological applications where distillation is not applicable. However, because most engineers with a BS degree are unfamiliar with these processes, they will be unlikely to consider sorption separations for new applications [79, p. 16].

Rationale – Education: Since the sorption separations are batch processes that require mass transfer calculations, they are inherently more difficult to understand than steady-state, equilibrium processes. Because many undergraduate chemical engineers have considerable difficulty understanding them, these processes will be taught mainly to graduate students.

Rationale – Research Funding: Money will be available for materials applications to make new sorbents, particularly if the research can be tied to nanotechnology. Biological applications have more sources of funding available than non-biological applications such as gas processing.

Fifth prediction: Crystallization will continue to be used in many industries where it is critically important. However, crystallization will remain an orphan without a home in the core of most undergraduate curricula. Crystallization research is currently underfunded and is unlikely to receive large increases.

Rationale – Industrial Use: Since many products are sold in a solid form, the final processing step is often crystallization. In addition, many products such as salts and other nonvolatile materials use very large-scale crystallization. These processes are not going to disappear.

Rationale – Education: Crystallization can be analyzed as an equilibrium staged separation, but the equilibrium is not the VLE that undergraduates and professors are familiar with. A complete analysis that predicts the crystal size distribution requires a mass transfer analysis coupled with population balances. This material is accessible to undergraduates, but because population balances are usually not covered elsewhere in the undergraduate curriculum, considerable time needs to be devoted to the topic. Because of competing pressures to cover other material, most schools will not carve out this time in the undergraduate core despite a call to make crystalline solids one of the core themes in the curriculum [35]. Thus, thorough analysis of crystallization will only be done in elective courses when there is a professor interested in teaching this material. Most ChE graduates have a weak background in crystallization and solids handling in general [79, p. 19], and this unfortunate condition is predicted to continue.

Rational – Research Funding: Much of the funding for crystallization was based on the promise of applications in space. This source appears to have largely dried up and no large-scale replacement sources have materialized.

Sixth prediction: Extraction will continue to be important in industry and to be covered in undergraduate courses, but not enough time and energy will be focused on the unique extraction design issues in education. No prediction will be made on research funding.

Rationale – Industrial Use: Extraction is very useful for cases where distillation does not work although the ratio of distillation to extraction units in industry is approximately 20 to 1 [79, p. 29]. Many of these applications of extraction such as separation of nonvolatile compounds are industrially important.

Rationale – Education: In many ways extraction is the most idiosyncratic equilibrium-staged separation process, although crystallization is a close second. Important content such as third-phase (or rag) formation and design of different types of extractors receives minimal or no coverage. Complete coverage of the methods used industrially would require a separate course. Because of time pressures on the curriculum, this will not happen in the required core. In addition, most current textbooks do not cover and most professors teaching separations are not familiar with these details.

Closure

Since reactors and separators are the core of chemical engineering, these aspects are important in the history, current practice and the future of chemical engineering. The history of separations helps explain how the current practice of chemical engineering separations and of separations in chemical engineering education evolved, and the history provides a useful, but probably limited, crystal ball to predict the future.

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