

## Mass Transfer: Yesterday, Today and Tomorrow

Recent archeological evidence suggests that mankind has been making alcoholic beverages for at least 9000 years. Although the records are sketchy, it looks like it took mankind about 7000 years to start using distillation to recover fractions with elevated alcohol concentrations. Man's obsession with alcohol has played a key role in the development of the art and science of distillation.

Although progress in the field of distillation could be considered to be slow, significant discoveries were made a long time ago. For instance: Anaxilaus of Thessaly was expelled from Rome in 28 BC for practicing magic: "There is sea-foam (salt) that has been heated in an earthenware wine-jar with new wine. When this has been boiled, if you apply a burning lamp to it, seizing the fire it sets itself alight, and if poured upon the head it does not burn at all." He stumbled upon the effect of changing the activity coefficients by the addition of salt, and that this yielded higher ethanol concentrations. 2000 years later engineers and scientists are working on processes to use salts in extractive distillation formulations to separate ethanol and water.

In the first 1000 years AD most of the somewhat sketchy records show distillation being used in the production of plant oils and the use of thermal decomposition to produce metals. It looks like this knowledge spread from the middle east and Egypt to Europe during this period. Similar techniques most likely also existed in India and China around the same time. There isn't clear evidence that the distillation of ethanol was practiced during this period, although the knowledge of Anaxilaus should have been available. Sometime during the 11<sup>th</sup> - 12<sup>th</sup> centuries the distillation of wine started in Italy and the knowledge spread to France and Spain, and later to Germany and England. One important impetus could have been the translation of Arabic medical works by Constantine at the medical school of Salerno. In the Vatican Consilia codex of 1276, Taddeo Alderotti of Florence (1215-1302) described the use of double distillation of wine to produce aqua vitae. This technique of using a batch still to recover ethanol drove distillation science for almost the next 500 years. In 1477 Hieronymus Braunschwygk published a book called *Liber de arte destillandi* on distilled "water" and its medicinal benefits. Scientists developed different condensers, and even stumbled upon the effect of reflux. They found that using extensions above the pot still increased the alcohol concentrations. This was due to internal reflux as a result of heat loss. In the 17<sup>th</sup> century the Neapolitan scientist, Della Porta, built his "seven headed hydra" that used internal reflux to create cuts of different alcohol concentrations. However, through all these centuries of distilling alcohol, it remained a batch operation and empty pipes carried the distillate to the receivers.

By the start of the 19<sup>th</sup> century things changed. In 1813 Cellier-Blumenthal was awarded a patent for a continuous distillation system (1808 invention) for the separation of ethanol and water. The tower was vertical, used reflux and had trays with bubble caps. Importantly, he heated the fresh wine with overhead material to improve the energy efficiency. In 1830 Coffey was granted a patent for a continuous distillation system for the separation of ethanol and water that used an internal condenser for generating reflux, and an external condenser to generate the overhead product. The feed exchanged heat with the bottoms, condensed to overhead product and served as the cooling medium in the internal condenser. The energy efficiency of this device was better than that of its predecessors. He also disclosed the use of sieve trays and trays with moveable valves in this tower.

Until the advent of coal tar chemistry in the first half of the 19<sup>th</sup> century and discovery of oil in 1859, the distillation of ethanol was the primary driver for the development of distillation technology and distillation

equipment. Continuous distillation knowledge from the world of ethanol was now available for producing products such as Anilin, Benzene, Phenol, tar and several other products.

In the late 1800's glass and porcelain random packing was used in several applications ranging from alcohol distillation to the distillation of oxygen and nitrogen (Linde). In 1913 Raschig patented the use of cylinders as random packing. In 1925 the McCabe-Thiele calculation method was introduced. 1935 saw the introduction of the concepts of HETP and HTU-NTU by Chilton and Colburn. In Germany the group of Kirshbaum extensively studied distillation in the 1930's to 1960's. In 1930 the first generation of structured packing (Spraypak) was introduced in the UK for the separation of isotopes. The concept of a dividing wall tower was introduced in 1939. It took until the 1980's for this technology to take off (BASF). In 1987 Kaibel (BASF) introduced the concept of multiple dividing walls in one tower.

Oil refining and the formation of companies such as BASF and DU PONT had a profound effect on distillation technology and distillation equipment.

Since world war II we saw the following developments: Cross-flow trays saw the introduction of improved moving valves, several generations of fixed valves, improved downcomer technology and a combination of features that increased both efficiency and capacity. New tray support structures were introduced, and the trays were designed to reduce the cost and installation time. All cross-flow trays are limited by the action of gravity. Centrifugal action trays were introduced to overcome the limitations of gravity. These trays could have as much as 60% more capacity than cross-flow trays. Rotating contactors, such as the HIGEE unit, was introduced to take this concept even further.

Structured packing saw the introduction of gauze packing in 1964, which yielded a very low pressure drop per theoretical stage. In 1977 sheet metal structured packing was introduced, which revolutionized the industry. It brought an affordable option for getting a large number of theoretical stages and a low pressure drop. The mid 1990's saw the introduction of high capacity structured packing. Subsequently further improvements were made to structured packing which yielded packing that significantly improved on the efficiency and capacity of the original structured packing.

Random packing saw the introduction of the Pall ring in the late 1940's, the IMTP® random packing in 1977, the Raschig Super Ring in the 1996 and the INTALOX® ULTRA random packing in 2006. The shapes of these random packing elements evolved to give higher capacity and efficiency for a given surface area of the packing.

Computational fluid dynamics were used since the 1990's to improve vapor and liquid inlets to the towers and to optimize distributors. Some of the improvements in the performance of packing and trays can also be ascribed to the improvements in distributors and inlet devices.

Process simulators became available on mainframe computers in the late 1970's and by the late 1980's made it to the desks of engineers with the proliferation of personal computers. The process simulators allowed engineers to rapidly explore alternatives, which yielded designs with lower capital and operating costs. Unfortunately, it also led to the garbage-in-garbage-out phenomenon.

Following the pioneering work of J.W. Gibbs since the 1870's, the work of Van der Waals (1870's) and Margules (1890's) laid the groundwork for the mathematical description of the liquid and vapor phase non-idealities that were needed to model the ever-increasing complexity of the chemical processes in the

process simulators. The work of Wilson, Prausnitz, Gmehling and a host of other very gifted people further enhanced the thermodynamic models used in modern day simulators.

#### Solvent driven separations

Anaxilius (28 BC) used sea salt to alter the activity coefficient of the ethanol-water system. This concept is exploited in modern-day extractive and azeotropic distillation. Extractive distillation is used on a very large scale in applications such as aromatics purification. Azeotropic distillation is used on a very large scale in alcohol drying. The benefit of these solvent systems mainly lies in the fact that the relative volatilities are modified to where much less energy is needed for the separation. Liqui-liquid extraction is an analogous unit operation which also relies on the modification of the activity coefficients by the solvent. The beauty of liquid extraction is that the phase split yields separation without the addition of energy. Liquid extraction can be combined with azeotropic and extractive distillation to yield very energy efficient separations of very complex mixture.

Membrane separations, such as pervaporation, have been combined with distillation, but the selectivity, cost and durability of the membranes have limited the application of this technology.

Adsorption technology has been combined with distillation in large-scale operations. A classic example of this technique is the use of adsorbents to break the azeotrope of ethanol and water to produce dry fuel alcohol.

Energy utilization has steadily become more of a hot button topic. This was even a topic in 1808 when Cellier-Blumenthal developed his continuous distillation concept. The use of pinch technology (Linnhoff) was developed in the 1970's to improve the overall energy utilization of plants and is still a very good tool. It has been recognized more than 50 years ago that distillation makes poor use of energy and that some energy integration in the towers could lead to reduced energy consumption. This led to several ways of addressing this problem. In the 1980's BASF started using the 40-year-old dividing wall technology to reduce capital and energy costs. Vapor recompression (heat pumps) was found to significantly reduce the energy consumption of close-boiling systems by compressing the overhead vapor to serve as a heating medium for the reboiler. Energy integration between the rectification and stripping sections led to the HIDIC concept. Recently the SUPER-HIDIC concept was commercialized which realized significant energy and capital savings.

For more than 200 years the challenges for scientists and engineers working in the field of distillation have been to reduce the capital cost and energy consumption of the units. Research and development in this field should thus be directed at equipment with higher capacity and efficiency, and processing schemes and solvent systems that can reduce the energy footprint of the distillation systems. The use of complementary unit operations, such as adsorption and membranes should be explored.

It has to be recognized that environmental responsibility and sustainability will keep on driving the use of chemicals and refined products down, but the growth in population and the growth in living standards will counteract these pressures. The volume of chemicals produced by distillation is immense and it will not be replaced by a different unit operation any time soon. As a distillation community we just have to continue to make distillation better. A key element in doing this is to have gifted people working in this field. Governments and universities will have to recognize that this centuries-old technology will need well-trained people for the foreseeable future and that the current level of funding for this training is insufficient.

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