

# DISTILLATION HANDBOOK

FOURTH EDITION

DH-187



A Siebe Group Company

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# I N T R O D U C T I O N

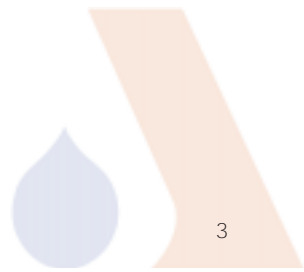
While the use of distillation dates back in recorded history to about 50 B.C., the first truly industrial exploitation of this separation process did not occur until the 12th century when it was used in the production of alcoholic beverages. By the 16th century, distillation also was being used in the manufacture of vinegar, perfumes, oils and other products.

As recently as two hundred years ago, distillation stills were small, of the batch type, and usually operated with little or no reflux. With experience, however, came new developments. Tray columns appeared on the scene in the 1820s along with feed preheating and the use of internal reflux. By the latter part of that century, considerable progress had been made. Germany's Hausbrand and France's Sorel developed mathematical relations that turned distillation from an art into a well defined technology.

Today, distillation is a widely used operation in the petroleum, chemical, petrochemical, beverage and pharmaceutical industries. It is important not only for the development of new products, but also for the recovery and reuse of volatile liquids. For example, pharmaceutical manufacturers use large quantities of solvents, most of which can be recovered by distillation with substantial savings in cost and pollution reduction.

While distillation is one of the most important unit operations, it is also one of the most energy intensive operations. It is easily the largest consumer of energy in petroleum and petrochemical processing, and so, must be approached with conservation in mind. Distillation is a specialized technology, and the correct design of equipment is not always a simple task.

This handbook describes APV's role in developing distillation systems, details different types of duties, discusses terminology and calculation techniques, and offers a selection of case studies covering a variety of successful installations.



# D I S T I L L A T I O N

Distillation, sometimes referred to as fractionation or rectification, is a process for the separating of two or more liquids. The process utilizes the difference of the vapor pressures to produce the separation.

Distillation is one of the oldest unit operations. While the first technical publication was developed in 1597, distillation already had been practiced for many centuries — specifically, for the concentration of ethyl alcohol for beverages. Today, distillation is one of the most used unit operations and is the largest consumer of energy in the process industries.

APV has been conducting business in the field of distillation since 1929. A brief history of APV in distillation is shown in **Figure 1**.

Today, APV mainly concentrates its marketing efforts in the area of solvent recovery, waste water stripping, chemical production and specialized systems, such as high vacuum systems for oils.

## A HISTORY OF APV IN DISTILLATION

1929	First Distillation Columns Manufactured
1933	West Tray License Obtained
1935	First Major APV Designed and Manufactured Distillation System
1935	Distillation Laboratory Established
1939	First Fuel Ethanol Distillation System
1939-45	Many Toluene/Benzene Systems Produced
1946	Acetic Acid Recovery System The Largest Order APV Had Ever Received
1969	Acquired L.A. Mitchell Group and Glitsch License for Valve Trays
1971	First Distillation System in USA
1990	The 100th U.S. Distillation System

*Figure 1. Brief history of APV distillation.*

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# A P V I N D I S T I L L A T I O N

## Complete Solutions for Your Distillation Requirements

### Process Technology

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- Conceptual Design
- Process Simulation
- Pilot Plant Testing
- 70 Years of Experience
- Process Guarantee

### Control Systems

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- Integration with Process Technology
- Functional Design Specification
- Foxboro Intelligent Automation

### Project Management

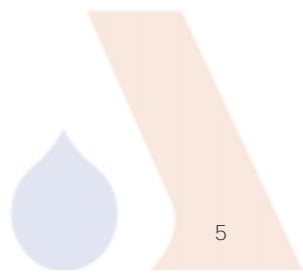
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- Project Engineering
- Equipment Fabrication
- Installation
- Training
- Start Up

### After Sales Service

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- Customer Service
- Troubleshooting
- Spare Parts



# BASIC PRINCIPLES OF DISTILLATION

When a mixture of two or more liquids is heated and boiled, the vapor has a different composition than the liquid. For example, if a 10% mixture of ethanol in water is boiled, the vapor will contain over 50% ethanol. The vapor can be condensed and boiled again, which will result in an even higher concentration of ethanol. Distillation operates on this principle.

Clearly, repeated boiling and condensing is a clumsy process, however, this can be done as a continuous process in a distillation column. In the column, rising vapors will strip out the more volatile component, which will be gradually concentrated as the vapor climbs up the column.

The vapor/liquid equilibrium (VLE) relationship between ethanol and water is shown in **Figure 2**. A similar relationship exists between all compounds. From this type of data, it is a relatively simple task to calculate the design parameters using one of the classical methods, such as McCabe-Thiele.

The key to this separation is the relative volatility between the compounds to be separated. The higher the relative volatility, the easier the separation and vice versa. For a binary system, the mole fraction  $y$  of component  $a$  in the vapor in equilibrium with the mole fraction  $x$  in the liquid is calculated from the following equation.

$$y_a = \frac{\alpha \cdot x_a}{1 + (\alpha - 1) \cdot x_a}$$

Where  $x_a$  is the mole fraction of  $a$  in the liquid and  $\alpha$  is the relative volatility.

The larger the relative volatility, the more easily the compound will strip out of water. For ideal systems which follow Raoult's law, the relative volatility is calculated by

$$\alpha = P_a/P_b$$

Where  $P_a$  and  $P_b$  are the vapor pressures of components  $a$  and  $b$  at a given temperature.

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The partial pressure  $p$  of component  $a$  above a binary ideal solution can be calculated by

$$p_a = P_a \cdot x_a$$

Where  $x_a$  is the mole fraction of component  $a$  in the liquid.

Similarly in a binary mixture, for component  $b$ .

$$p_b = P_b \cdot x_b$$

Notice that the sum of the partial pressures must equal the total system pressure:  $P = p_b + p_a$ . For non ideal mixtures (usually the case with steam stripping duties), the partial pressure is calculated from

$$P_a = \gamma_a P_a^s x_a$$

$$P_b = \gamma_b P_b^s x_b$$

Where  $\gamma$  is the activity coefficient of the compound. The activity coefficient essentially quantifies the deviation from ideality.

For multicomponent mixtures, the mathematical representation of the VLE becomes more complex. It is necessary to use complex equations to predict the performance. The simplification commonly used as a substitute for the rigorous equations is **K value**.  $y_a = K x_a$ . The ratio of the **K value** of different components reflects the relative volatilities between those components.

It is not the intention of this publication to discuss methods for calculating a distillation system. Classical graphical calculations have been the McCabe-Thiele method, using the data shown in **Figure 2**, and the Ponchon Savarit method, which is more accurate and uses an enthalpy diagram, as shown in **Figure 3**, as well as the VLE data.

All these graphical methods have been rendered obsolete by the various process simulation programs, such as SimSci. Even with these highly sophisticated programs, there is still a need for test work on many systems. For ideal mixtures, which are rare, the program will provide a theoretically correct solution. For non ideal mixtures, the program can only make estimates by using thermodynamic equations such as UNIFAC. Experimental data can be used for more precise solutions. A considerable amount of experimental data, however, is in the program database.

(1) ETHANOL ----- C2H6O  
 (2) WATER ----- H2O

+++++ ANTOINE CONSTANTS REGION +++++  
 (1) 8.11220 1592.864 226.104 20- 93 C  
 (2) 8.07131 1730.630 233.426 20- 100 C

CONSISTENCY  
 METHOD 1 -  
 METHOD 2 +

PRESSURE- 760.00 MM HG ( 1.013 BAR )  
 LT: DALAGER P., J. CHEM. ENG. DATA 14,298 (1969).

CONSTANTS: A12 A21 ALPHA12  
 MARGULES 1.7577 0.7243  
 VAN LAAR 1.7850 0.8978  
 WILSON 419.1380 911.1302  
 NRTL -222.4277 1557.2947 0.2862  
 UNIQUAC -94.6899 427.5173

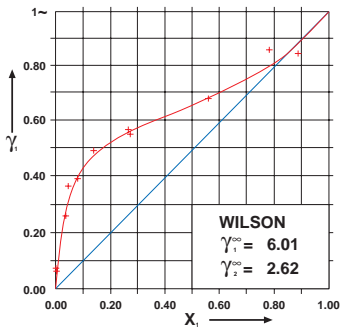


Figure 2.

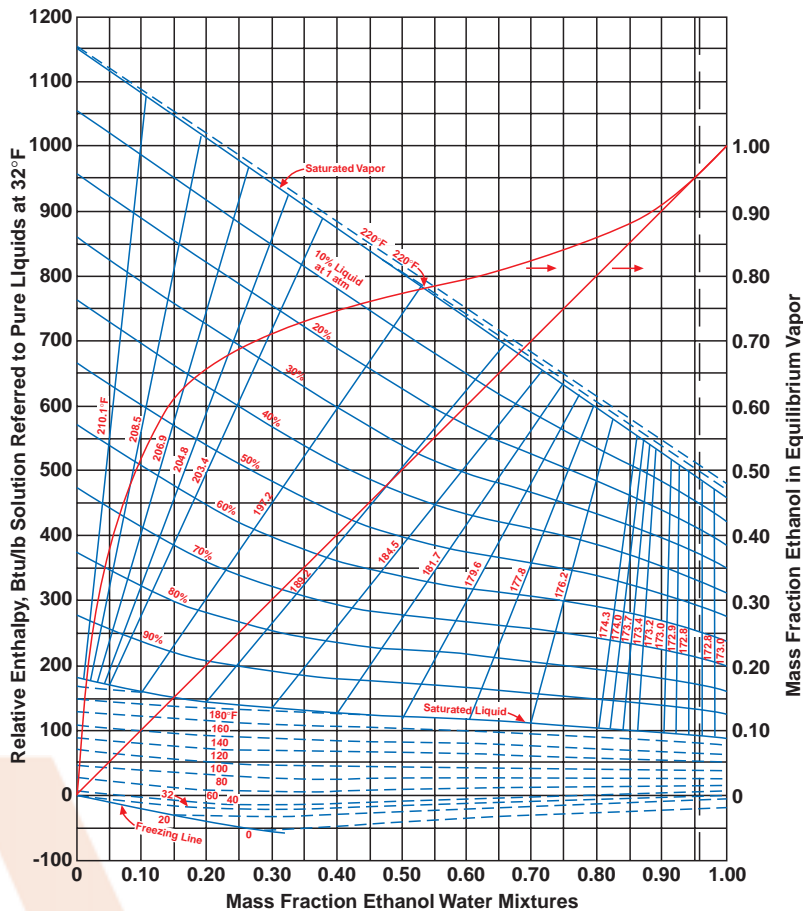


Figure 3. Calculations by enthalpy-composition diagram.



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# D I S T I L L A T I O N T E R M I N O L O G Y

*To provide a better understanding of the distillation process, the following briefly explains the terminology most often encountered.*

## SOLVENT RECOVERY

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The term “solvent recovery” often has been a somewhat vague label applied to the many different ways in which solvents can be reclaimed by industry.

One approach employed in the printing and coatings industries is merely to take impure solvents containing both soluble and insoluble particles and evaporate the solvent from the solids. For a duty of this type, APV offers the Paraflash evaporator, a compact unit which combines a Paraflow plate heat exchanger and a small separator. As the solvent laden liquid is recirculated through the heat exchanger, it is evaporated and the vapor and liquid are separated. This will recover a solvent, but it will not separate solvents if two or more are present.

Another technique is available to handle an air stream that carries solvents. By chilling the air by means of vent condensers or refrigeration equipment, the solvents can be removed from the air stream.

Solvents also can be recovered by using extraction, adsorption, absorption and distillation methods.

## SOLVENT EXTRACTION

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Essentially a liquid/liquid process where one liquid is used to extract another from a secondary stream, solvent extraction generally is performed in a column somewhat similar to a normal distillation column. The primary difference is that the process involves the mass transfer between two liquids instead of a liquid and a vapor.

During the process, the lighter (i.e., less dense) liquid is charged to the base of the column and rises through packing or trays while the more dense liquid descends. Mass transfer occurs and one or more components is extracted from one stream and passed to the other.



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Liquid/liquid extraction sometimes is used when the breaking of an azeotrope is difficult or impossible by distillation techniques.

## CARBON ADSORPTION

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The carbon adsorption technique is used primarily to recover solvents from dilute air or gas streams.

In principle, a solvent laden air stream is passed over activated carbon and the solvent is adsorbed into the carbon bed. When the bed becomes saturated, steam is used to desorb the solvent and carry it to a condenser. In such cases as toluene, for example, recovery of the solvent can be achieved simply by decanting the water/solvent two phase mixture which forms in the condensate. Carbon adsorption beds normally are used in pairs so that the air flow can be diverted to the secondary bed when required.

On occasion, the condensate is in the form of a moderately dilute miscible mixture. In this case, the solvent must be recovered by distillation. This would apply especially to water miscible solvents such as acetone.

## ABSORPTION

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When carbon adsorption cannot be used because certain solvents either poison the activated carbon bed or create so much heat that the bed can ignite, absorption offers an alternate technique. Solvent is recovered by pumping the solvent laden air stream through a column countercurrently to a water stream, which absorbs the solvent. The air from the top of the column essentially is solvent free, while the dilute water/solvent stream discharged from the column bottom usually is concentrated in a distillation column. Absorption also can be applied in cases where an oil rather than water is used to absorb certain organic solvents from the air stream.

## AZEOTROPES

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During distillation, some components form an azeotrope at a certain stage of the fractionation, requiring a third component to break the azeotrope and achieve a higher percentage of concentration. In the case of ethyl alcohol and water, for

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example, a boiling mixture containing less than 96% by weight ethyl alcohol produces a vapor richer in alcohol than in water and is readily distilled. At the 96% by weight point, however, the ethyl alcohol composition in the vapor remains constant (i.e., the same composition as the boiling liquid). This is known as the azeotrope composition and further concentration requires use of a process known as azeotropic distillation. Other common fluid mixtures which form azeotropes are formic acid/water, isopropyl alcohol/water, and iso butanol/water.

## AZEOTROPIC DISTILLATION

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In a typical azeotropic distillation procedure, a third component, such as benzene, isopropyl ether or cyclohexane, is added to an azeotropic mixture, such as ethyl alcohol/water, to form a ternary azeotrope. Since the ternary azeotrope is richer in water than the binary ethyl alcohol/water azeotrope, water is carried over the top of the column. The ternary azeotrope, when condensed, forms two phases. The organic phase is refluxed to the column while the aqueous phase is discharged to a third column for recovery of the entraining agent.

Certain azeotropes such as the n-butanol/water mixture can be separated in a two column system without the use of a third component. When condensed and decanted, this type of azeotrope forms two phases. The organic phase is fed back to the primary column and the butanol is recovered from the bottom of the still. The aqueous phase, meanwhile, is charged to the second column with the water being taken from the column bottom. The vapor streams from the top of both columns are condensed and the condensates run to a common decanter.

## EXTRACTIVE DISTILLATION

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This technique is somewhat similar to azeotropic distillation in that it is designed to perform the same type of task. In azeotropic distillation, the azeotrope is broken by carrying over a ternary azeotrope at the top of the column. In extractive distillation, a higher boiling compound is added and the solvent to be recovered is pulled down the column and removed as the bottom product. A further distillation step is then required to separate the solvent from the entraining agent.



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## STRIPPING

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In distillation terminology, stripping refers to the removal of a volatile component from a less volatile substance. Again, referring to the ethyl alcohol/water system, stripping is done in the column below the feed point, where the alcohol enters at about 10% by weight and the resulting liquid from the column base contains less than 0.02% alcohol by weight. This is known as the stripping section of the column. This technique does not increase the concentration of the more volatile component, but rather decreases its concentration in the less volatile component.

A stripping column also can be used when a liquid such as water contaminated by toluene cannot be discharged to sewer. For this pure stripping duty, the toluene is removed within the column, while vapor from the top is decanted for residual toluene recovery and refluxing of the aqueous phase.

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## RECTIFICATION

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For rectification or concentration of the more volatile component, the top section of a column above the feed point is required. By means of a series of trays and with reflux back to the top of the column, a solvent such as ethyl alcohol can be concentrated to over 95% by weight.

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## BATCH DISTILLATION

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When particularly complex or small operations require recovery of the more volatile component, APV can offer batch distillation systems of various capacities. Essentially a rectification type process, batch distillation involves pumping a batch of liquid feed into a tank where boiling occurs. Vapor rising through a column above the tank combines with reflux coming down the column to effect concentration. This approach is not too effective for purifying the less volatile component since there is only the equivalent of one stripping stage.

For many applications, batch distillation requires considerable operator intervention or alternatively, a significant amount of control instrumentation. While a batch system is more energy intensive than a continuous system, steam costs generally are less significant on a small operation. Furthermore, it is highly flexible and a single batch column can be used to recover many different solvents.

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## CONTINUOUS DISTILLATION

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The most common form of distillation used by the chemical, petroleum and petrochemical industries is the continuous mode system.

In continuous distillation, feed constantly is charged to the column at a point between the top and bottom sections. The section above the feed point rectifies or purifies the more volatile component while the column section below the feed point strips out the more volatile from the less volatile component. In order to separate  $N$  components with continuous distillation, a minimum of  $N-1$  distillation columns is required.

Sidedraws can be taken to remove extra streams from the column but only when high purity of individual components is not required.

## TURNDOWN

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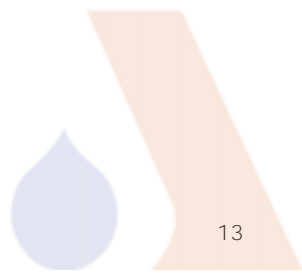
The turndown ratio of a column is an indication of the operating flexibility. If a column, for example, has a turndown ratio of 3, it means that the column can be operated efficiently at 33% of the maximum design throughput.

## STEAM STRIPPING

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The term steam stripping can be applied to any system where rising steam vapors in a column strip out the volatile components in the liquid. In particular, the term is applied to systems where steam is used to strip out partially miscible organic chemicals, even though the organic chemicals have boiling points above water. For example, toluene, which has a boiling point of  $110^{\circ}\text{C}$ , can be stripped out of water with steam. The low solubility of toluene in water changes the activity coefficient, and the toluene can be stripped off as the water/toluene azeotrope.

APV has sold many steam strippers, which will be discussed later.



# S Y S T E M C O M P O N E N T S

*The following descriptions briefly define the many components required for a distillation system, as well as the many variations in components that are available to meet different process conditions.*

## COLUMN SHELLS

A distillation column shell can be designed for use as a free-standing module or for installation within a supporting steel structure. Generally speaking, a self-supporting column is more economical at diameters of 4 ft (1.2m) or larger. This holds true even under extreme seismic-3 conditions.

APV has built distillation columns in carbon steel, 304 stainless steel, 316 stainless steel, Monel, titanium, Hastelloy C and Incoloy 825. Usually, it is more economical to fabricate columns in a single piece without shell flanges. This technique not only simplifies installation but also reduces the danger of leakage during operation. Columns over 80 ft (24m) in length have been shipped by road without transit problems.

While columns of over 3 ft (0.9m) in diameter normally have been transported without trays to prevent dislodgment and possible damage, recent and more economical techniques have been devised for factory installation of trays with the tray manways omitted. After the column has been erected, manways are added and, at the same time, the fitter inspects each tray.

With packed columns of 24 inch (600 mm) diameter or less which may use high efficiency sheet metal or mesh packing, the packing can be installed prior to shipment. Job site packing installation, however, is the norm for larger columns. This prevents the packing from bedding down during transit and leaving voids that would reduce operating efficiency. Random packing always is installed after delivery, except for those rare occasions when a column can be shipped in a vertical position.

Access platforms and interconnecting ladders designed to OSHA standards also are supplied for on site attachment to free-standing columns.

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Installation usually is quite simple since columns are fitted with lifting lugs. At the fabrication stage, a template is drilled to match support holes in the column base ring. With these exact template dimensions, supporting bolts can be preset for quick and accurate coupling as the column is lowered into place.

## COLUMN INTERNALS

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During recent years, the development of sophisticated computer programs and new materials has led to many innovations in the design of trays and packings for more efficient operation of distillation columns. In designing systems for chemical, petroleum and petrochemical use, APV specialists take full advantage of available internals to assure optimum distillation performance.

## TRAY DEVICES

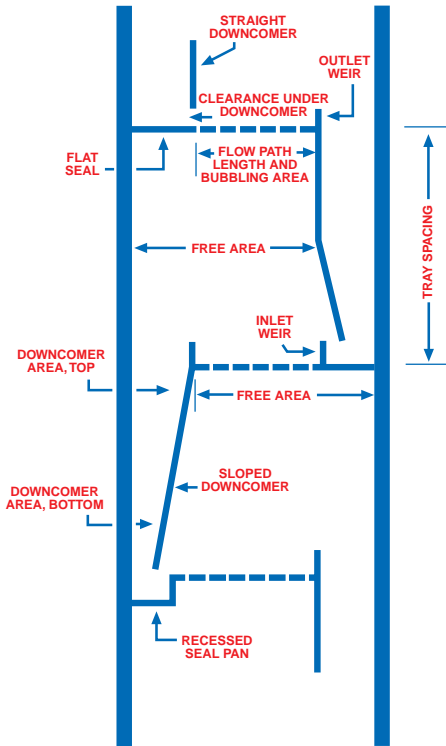
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While there are perhaps five basic distillation trays suitable for industrial use, there are many design variations of differing degrees of importance and a confusing array of trade names applied to their products by tray manufacturers. The most modern and commonly used devices include sieve, valve, bubble cap, dual flow, and baffle trays – each with its advantages and preferred usage. Of these, the sieve and valve type trays currently are most often specified.

For a better understanding of tray design, **Figure 4** defines and locates typical tray components. The material of construction usually is 14 gauge with modern trays adopting the integral truss design which simplifies fabrication. A typical truss tray is shown in **Figure 5**. For columns less than 3 ft (0.9m) in diameter, it is not possible to assemble the truss trays in the column; therefore, trays must be preassembled on rods into a cartridge section for loading into the column.

**Figure 6** shows this arrangement in scale model size.

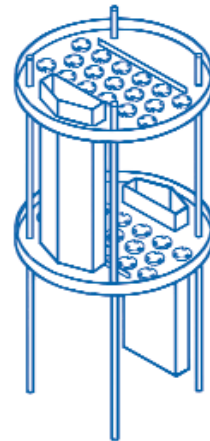
The hydraulic design of a tray is a very important factor. The upper operating limit generally is governed by the flood point, although in some cases, entrainment also can restrict performance before the onset of flooding. Flooding is usually caused by either massive entrainment, termed jet flooding, or by downcomer back-up. Downcomer back-up occurs when a tray design provides insufficient downcomer area to allow for the liquid flow or when the pressure drop across the



**Figure 4.** Tray component terminology.



**Figure 5.** Typical tray of integral truss design.



**Figure 6.** Cartridge tray assembly.

tray is high, which forces liquid to back up in the downcomer. When the downcomer is unable to handle all the liquid involved, the trays start to fill and pressure drop across the column increases. This also can occur when a highly foaming liquid is involved. Flooding associated with high tray pressure drops and small tray spacing takes place when the required liquid seal is higher than the tray spacing. Downcomer design also is particularly important at high operating pressure due to a reduction in the difference between vapor and liquid densities.

The lower limit of tray operation, meanwhile, is influenced by the amount of liquid weeping from one tray to the next. Unlike the upward force of entrainment, weeping liquid flows in the normal direction and considerable amounts can be tolerated before column efficiency is significantly affected. As the vapor rate decreases, however, a point eventually is reached when all the liquid is weeping



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and there is no liquid seal on the tray. This is known as the dump point, below which there is a severe drop in efficiency.

## SIEVE TRAY

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The sieve tray is a low cost device which consists of a perforated plate that usually has holes of  $3/16$  inch to 1 inch (5 to 25mm) diameter, a downcomer, and an outlet weir. Although inexpensive, a correctly designed sieve tray can be comparable to other styles in vapor and liquid capacities, pressure drop and efficiency. For flexibility, however, it is inferior to valve and bubble cap trays. It is also sometimes unacceptable for low liquid loads when weeping has to be minimized.

Depending on process conditions, tray spacing and allowable pressure drop, the turndown ratio of a sieve tray can vary from 1.5 to 2, and occasionally higher. For many applications, a turndown of 1.5 is acceptable.

It also is possible to increase the flexibility of a sieve tray for occasional low throughput operation by maintaining a high vapor boilup and increasing the reflux ratio. This may be economically desirable when the low throughput occurs for a small fraction of the operating time. Flexibility, likewise, can be increased by the use of blanking plates to reduce the hole area. This is particularly useful for initial operation when it is proposed to increase the plant capacity after a few years. There is no evidence to suggest that blanked-off plates have inferior performance to unblanked plates of similar hole area.

## DUAL FLOW TRAY

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The dual flow tray is a high hole area sieve tray without a downcomer. The liquid passes down the same holes through which the vapor rises. Since no downcomer is used, the cost of the tray is lower than that of a conventional sieve tray. In addition, the less complex design allows for easier cleaning.

In recent years, use of the dual flow tray has declined somewhat because of difficulties experienced with partial liquid/vapor bypassing of the two phases, particularly in larger diameter columns. The dual flow column also has a very restricted operating range and a reduced efficiency because there is no crossflow of liquid.

## VALVE TRAY

While the valve tray dates back to the rivet type first used in 1922, many design improvements and innumerable valve types have been introduced in recent years. Two types of valves are illustrated in **Figure 7**. These valves provide the following advantages:

1. Throughputs and efficiencies can be as high as sieve or bubble cap trays.
2. Very high flexibility can be achieved and turndown ratios of 4 to 1 can be obtained without having to resort to large pressure drops at the high end of the operating range.
3. Special valve designs with venturi shaped orifices are available for duties involving low pressure drops.
4. Although slightly more expensive than sieve trays, the valve tray is economical in view of its numerous advantages.
5. Since an operating valve is continuously in movement, the valve tray can be used for light to moderate fouling duties. APV has successfully used valve trays on brewery effluent containing waste beer, yeast and other materials with fouling tendencies.



**Figure 7.**

*(Left) Special two-stage valve with lightweight orifice cover for complete closing.*

*(Below) Typical general purpose valve which may be used in all types of services.*



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## BUBBLE CAP TRAY

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Although many bubble cap columns still are in operation, bubble cap trays rarely are specified today because of high cost factors and the excellent performance of the modern valve tray. The bubble cap, however, does have a good turndown ratio and is good for low liquid loads.

## BAFFLE TRAY

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Baffle trays are arranged in a tower in such a manner that the liquid flows down the column by splashing from one baffle to the next tower baffle. The ascending gas or vapor, meanwhile, passes through this "curtain" of liquid spray.

Although the baffle tray has a low efficiency, it can be useful in applications when the liquid contains a high fraction of solids.

## PACKINGS

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For many types of duties, particularly those involving small diameter columns, packing is the most economical tower internal. One advantage is that most packing can be purchased from stock on a volumetric basis. In addition, the mechanical design and fabrication of a packed column is quite simple. Disadvantages of packing include its unsuitability for fouling duties, breakage of ceramic packing, and in APV experience, less predictive performance, particularly at low liquid loads or high column diameters.

The most widely used packing is the random packing, usually Rashig Rings, Pall Rings and ceramic saddles. These are available in various plastics, a number of different metals and, with the exception of Pall Rings, in ceramic materials. While packings in plastic have the advantage of corrosion resistance, the self-wetting ability of some plastic packing such as fluorocarbon polymers sometimes is poor, particularly in aqueous systems. This considerably increases the HETP when compared with equivalent ceramic rings.

Structured high efficiency packings have become more available in the last 20 years. These packings, which are usually made of corrugated gauze or sheet metal, can provide better efficiency than random packing, but at a higher cost.

The gauze packings can provide an HETP of 8 to 10 in (200 to 250mm) for organic systems. A sample of gauze packing is shown in **Figure 8**. The sheet metal packings usually have an HETP in the range of 18 to 22 in (450mm to 550mm), but are far less expensive than the gauze. These types of packing are good at maintaining distribution of the liquid.

With both random and, in particular, high efficiency packing, considerable attention must be given to correct liquid and vapor distribution. Positioning of the vapor inlets and the design of liquid distributors and redistributors are important factors that should be designed only by experts.



*Figure 8. Segment of high efficiency metal mesh packing.*

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## AUXILIARY EQUIPMENT

In any distillation system, the design of auxiliary equipment such as the reboiler, condenser, preheaters and product coolers is as important as the design of the column itself.

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## REBOILER

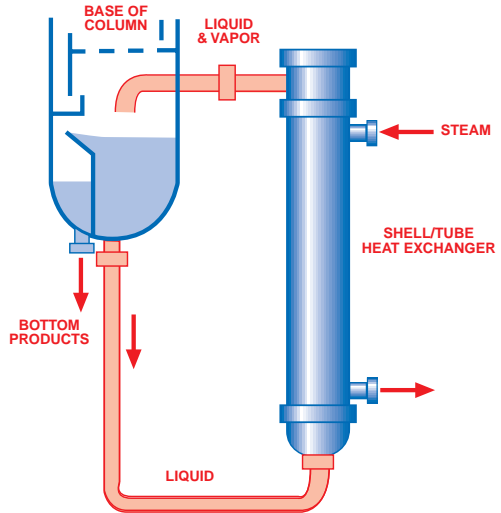
Although there are many types of reboilers, the shell and tube thermosyphon reboiler is used most frequently. Boiling within the vertical tubes of the exchanger produces liquid circulation and eliminates the need for a pump. A typical arrangement is shown in **Figure 9**.

For certain duties, particularly when the bottoms liquid has a tendency to foul heat transfer surfaces, it is desirable to pump the liquid through a forced circulation reboiler. Since boiling can be suppressed by use of an orifice plate at the outlet of the unit, fouling is reduced. The liquid being pumped is heated under pressure and then is flashed into the base of the column where vapor is generated.

An alternate approach is the use of a plate heat exchanger as a forced circulation reboiler.

With this technique, the very high liquid turbulent flow which is induced within the heat exchanger through the use of multiple corrugated plates holds fouling to a minimum. Meanwhile, the superior rates of heat transfer that are achieved reduces the surface area required for the reboiler.

*Figure 9. Typical shell and tube thermosyphon reboiler arrangement.*



## CONDENSERS

Since most distillation column condensers are of shell and tube design, the processor has the option of condensing on either the shell or tube side. From the process point of view, condensation on the shell side is preferred since there is less subcooling of condensate and a lower pressure drop is required. These are important factors in vacuum duties. Furthermore, with cooling water on the shell side, any fouling can be removed more easily.

Tube side condensation, on the other hand, can be more advantageous whenever process fluid characteristics dictate the use of more expensive, exotic materials. Capital cost of the unit can be reduced by using a carbon steel shell.

## PREHEATERS/COOLERS

The degree to which fluids are aggressive to metals and gasketing materials generally determines the selection of plate or shell and tube preheaters and product coolers.

If fluids are not overly aggressive toward gasket materials, a plate heat exchanger is an extremely efficient preheater since a very close temperature approach may be achieved. Added economy is realized by using heat from the top and bottoms product for all necessary preheating.

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While plate type units can be supplied with fluorocarbon gaskets, very aggressive duties normally are handled in a number of tubular exchangers arranged in series to generate a good mean temperature difference. The use of multiple tubular units is more expensive than a single plate heat exchanger but is unavoidable for certain solutions such as aromatic compounds.

One technique that makes use of the plate heat exchanger with gasket aggressive fluids is a welded plate pair. In this case, one of the fluids is contained between a pair of plates that are laser welded. Since the 'O' ring gaskets around the ports on the non welded plates can be supplied in PTFE, it is possible to handle the aggressive fluid. However, this is only possible on one side of the exchanger, so the second fluid must be free of aggressive fluids. This is often the type of duty that is required for a waste water steam stripper where the organics are stripped out of the contaminated feed, and are no longer present in the hot bottoms product.

## VENT CONDENSERS

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It is normal practice on distillation systems to use a vent condenser after the main condenser to minimize the amount of volatiles being driven off into the atmosphere. Usually of the shell and tube type, the vent condenser will have about one-tenth the area of the main unit. The vent condenser will utilize a colder cooling medium than that of the main condenser to cool the non-condensable gases to about 50°F (10°C).

## PUMPS

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Since most distillation duties involve fluids that are highly flammable and have a low flash point, it is often essential that explosion-proof (Class 1, Group D, Division 1) pump motors be supplied. Centrifugal pumps generally are specified since they are reliable and can provide the necessary head and volumetric capacity at moderate costs.

For environmental purposes, it is often necessary to supply a pressurized oil seal pot with the oil recirculated around the pump, as well as a pumping ring inside the seal itself to minimize the leaking of the process fluid into the environment. These are extremely expensive, but often necessary, seals.

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# S T E A M S T R I P P I N G

One of the most effective and flexible techniques for the removal of volatile organic chemicals from waste water, is to strip out the compounds using steam in a distillation column. While this has been a well known technique for many decades, in recent years it has been developed for the removal of VOCs to extremely low concentrations. This technique is classified as best demonstrated available technology (BDAT). Steam stripping is effective at stripping out most VOCs from water in a wide range of concentrations. It is particularly economical at the higher organic concentrations in aqueous streams, where steam can also be used directly to recover, as well as remove, VOCs. The process can strip the VOCs to extremely low concentrations in one operation without a large increase in costs. For example, the difference in capital costs to strip benzene, toluene or xylene (BTX) from a contaminated water stream to 20 ppb compared with 200 ppb would be small. There would be no increase in operating costs.

## PRINCIPAL OF OPERATION

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For water miscible and water immiscible high volatile compounds, the process is a relatively straight forward distillation system. For many of the systems, vapor liquid equilibrium data are available in the literature and in the many process simulation software programs.

Steam stripping can also be used to remove low volatile components when the components have low miscibility with water. Those compounds can all be effectively removed from water by steam stripping, even though they have a lower volatility than water. This technique has been used for many years, particularly in the petroleum industry, where the presence of steam with low miscibility organics has allowed for high boiling compounds to be distilled at lower temperatures. Due to the low solubility in water, the activity coefficient is greatly increased and the compound forms a low boiling point azeotrope with water. The lower the solubility, the higher the enhancement of the activity coefficient. A general rule is that the ease of stripping of any VOC is directly proportional to its volatility, and inversely proportional to its solubility in water. This is a most important characteristic



*Figure 10. Two steam strippers.*

since, in practice, it enables some high boiling toxic compounds such as PCBs to be removed by steam stripping.

High boiling, fully water miscible compounds cannot be removed by steam stripping. In these cases the water can be removed as distillate from a distillation process, but this will require considerably more energy and/or more capital cost.

## PROCESS DESCRIPTION

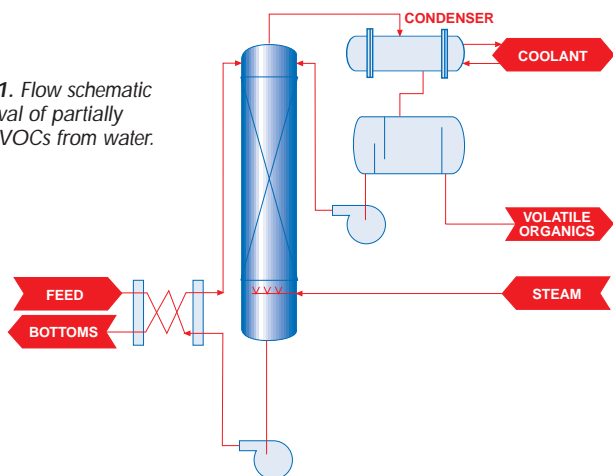
A flow schematic for the removal of partially miscible VOCs from water is shown in **Figure 11**.

Waste water under flow control is pumped through a preheater where it is regeneratively heated using the hot column bottoms. The water then enters the column, usually at or close to the top. The water flows down the column where it is contacted by rising steam. To provide for good vapor/liquid contact, the column contains either distillation trays or packing. Typically, a stripper of this type would require about 20 actual distillation trays or the equivalent in packing. Steam is supplied at the base of the column by either direct sparge, as shown, or by using a reboiler.

The steam strips out the VOCs, which are carried over and condensed. The liquid from the condenser flows into a decanter. Since the liquids are only partially soluble, and since the VOCs are concentrated in the column, the liquid separates



**Figure 11.** Flow schematic for removal of partially miscible VOCs from water.



into two distinct phases. Depending on whether the organic material is heavier or lighter than water, the product is removed as either the light phase (as shown on the schematic) or as the heavy phase. The aqueous phase which contains organics at the solubility limit is refluxed back to the column.

The process, therefore, produces clean water at the bottom and a concentrated organic liquid, albeit saturated with water, at the top. In the case of a binary mixture, the organic compound can be recycled back to the process. In other cases there is a multicomponent liquid mixture which can be recovered by subsequent distillation. Or, if quantities are too small for economic recovery, the VOCs can be incinerated or shipped to a waste processor.

In many cases the organics present are not limited to low miscibility liquids. The presence of water miscible compounds such as acetone or methanol is often the case. With this situation, the process is more complicated and usually requires more energy and equipment. These compounds act as co-solvents which effectively lower the activity coefficients of the partly water miscible compounds. The removal of those compounds now requires more steam, which not only increases operating costs, but also equipment size and cost. A further problem occurs: co-solvency usually means that the organics cannot be separated from water in a decanter because the overhead is single phase. The decanter, which otherwise is an extremely efficient separation device, cannot operate. It is then necessary to incorporate a rectification section on the top of the column in order to concentrate the organics and minimize water in the overhead. The system is now a complete distillation process which, although fully effective, is also more expensive.

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# S O L V E N T R E C O V E R Y

Many plants, such as pharmaceutical, printing, explosives, electronic and chemical, generate waste solvents that must be either shipped away for disposal or recovered.

There are many parameters to be addressed to determine the feasibility of solvent recovery. The most important parameters are:

- Prices of solvents to be recovered.
- Costs of disposal of solvents if not recovered.
- Capital and operating costs of a solvent recovery system.
- Achievable purity of recovered solvents.

There are also less tangible benefits to recovery. For example, when the solvents are recovered, there is no potential liability for solvents shipped out for disposal. Also, the recovery reduces the vulnerability to shortages and price increases.

A number of separation techniques can be used for recovery, depending on the composition of the waste. If the solvent has only to be recovered from a solid, then the recovery can be performed by evaporation. If the solvent is in an air or gas stream, then the solvent can be recovered by refrigeration and/or by carbon adsorption. When solvents are mixed and need to be recovered and purified, the process becomes quite complicated. The most important technique for this recovery is distillation. Other techniques are generally only used when a separation by distillation is either difficult or impossible.

Solvents can be recovered by continuous or batch distillation. The selection is dependent on the complexity of the mixture and the volumes to be processed.

If the separation is fairly simple, such as a ternary or binary mixture, and the volume to be recovered is quite high, it may be best to use continuous distillation. This type of distillation minimizes energy. Also for large duties, energy can be saved by operating in multi-effect mode. A two-effect isopropyl alcohol recovery system is shown in **Figure 12**.

The principle operation of continuous solvent distillation is the same as described under steam stripping, which is one type of distillation process. A typical



**Figure 12.** Two-effect isopropyl alcohol recovery system.

continuous distillation column has two sections. One section below the feed is referred to as the stripping section. This is where the light components in the feed are stripped out of the heavy components to produce a bottoms product with small quantities of the light components. The section above the feed is the rectification section, where the light components are concentrated. Many steam strippers do not include a rectification section, since with partially miscible components, an effective concentration can be obtained merely by decanting.

For solvent recovery, batch distillation is still the most common technique used for the purification of solvents. Although in the process industries, most distillation systems are continuous, batch systems are preferred for the distillation of relatively

small quantities of solvents. Also, to separate a multi-component mixture of  $n$  components by continuous distillation, a minimum of  $n-1$  separate columns are required, which involves a significantly higher capital cost. A batch system can often separate many components in one column, albeit with a premium on utilities.

The design of a batch distillation system is usually extremely complicated and best left to experts in the field. The multicomponent nature of the feed, coupled with the added parameter of time, (which is not a factor with continuous distillation), results in complex calculations. While there are a number of hand calculation techniques, a far easier and more accurate technique is to use one of the process simulator computer programs that are available from Simulation Sciences (BatchSim™).

While it is not proposed here to detail the theory of batch distillation, it is important to look at some of the general parameters involved.

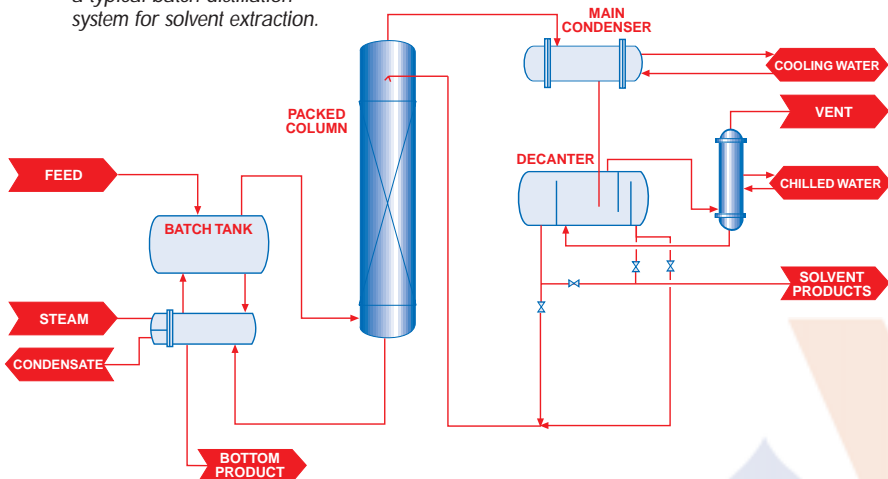


**Figure 13.** Batch distillation system.

For a mixture of 2, 3, or even 4 solvents, batch distillation will enable the user to recover solvents at high purity, providing there are no azeotropes present. For mixtures containing many components, it will usually only be economical to recover the dominant and/or the most expensive components. For example, a solution containing over 5 components in relatively equal proportions may not be worth processing.

A flow schematic of a typical batch distillation system is shown in **Figure 14**. Waste solvents from the feed tank are pumped into the batch tank. When the tank is about 80% full, the feed is stopped and the contents of the batch tank are heated to boiling by the heating medium in the reboiler. Once the mixture starts to boil, vapor is carried up the column and is condensed in the overhead condenser. The condensate flows either to a reflux drum or to a decanter (as shown). Reflux is then pumped back to the top of the column. At start up, the system is operated at total reflux until the required purity of the most volatile component is achieved. At this point the product is withdrawn at a rate controlled by reflux ratio. The reflux ratio is set according to data from an on-line analyzer or temperature profile in the column. When the reflux ratio becomes too high (typically 15 or 30 to 1), then it is no longer economical to continue to produce a top product. The flow is diverted to a slop out tank, and the reflux ratio is reduced. Eventually the most

**Figure 14.** Flow schematic of a typical batch distillation system for solvent extraction.



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volatile component will be completely driven off. The steps can be repeated for each volatile component required to be recovered. The system illustrated shows a reversible decanter so that either the heavy or light phase can be refluxed, or the decanter can be used merely as a reflux tank.

The advantage of batch distillation is the added dimension of time, which allows multiple cuts to be taken from the top of the column. Thus, the components can be taken off as products in order of their volatility. In addition, the process can be stopped at any time to allow for the addition of a further component for use as an extraction agent. The main disadvantage of batch distillation is that it essentially has only one theoretical stripping stage. It is a rectification process. Therefore, this is an inefficient process when it is required to recover the least volatile component at high purity. However, this is not usually the case with VOC recovery, since bottoms water contaminated with small quantities of solvent can be recycled back to the steam stripper.

# D I S T I L L A T I O N

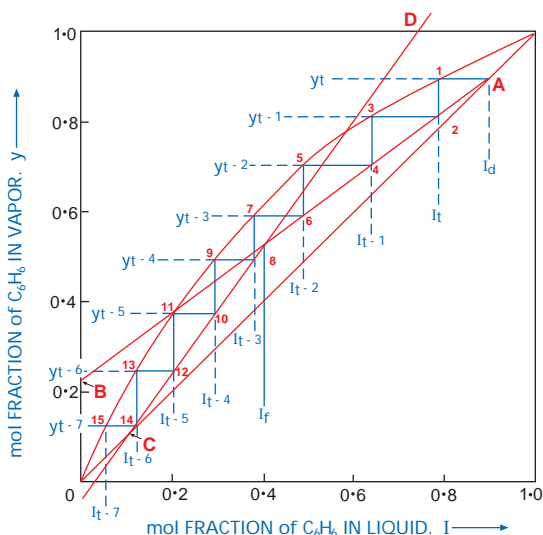
# C O L U M N C O N T R O L

## PHILOSOPHY

The control of distillation columns can be relatively complex when compared with many other unit operations. In particular, the control of continuous distillation systems is most difficult. The reasons are:

- In many systems there are multi-component mixtures which are difficult and/or expensive to analyze on-line.
- The vapor/liquid flows in the column must be maintained relatively constant to satisfy vapor/liquid equilibrium conditions.
- The mass balance must also be maintained so that the removal rate of all components is equal to their respective feed rate.
- There can be more than one column operating in series.

In order to simplify the problem, it is necessary to consider the conditions in a single column operating with a binary mixture. The classical McCabe-Thiele graphical simulation shown in **Figure 15** is a good illustration of the problem. The designer of the system has calculated the reflux ratio and the number of theoretical

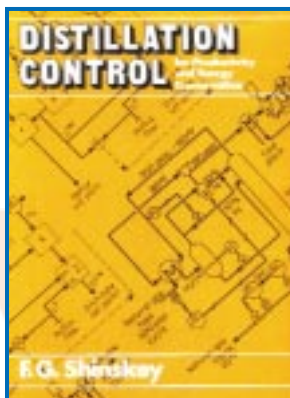


**Figure 15.** Determination of the number of plates by the McCabe-Thiele method.

plates required to produce the separation. The number of theoretical plates are then converted to actual trays, or an equivalent packing height for the final column design. In order for this column to produce the design separation, it is essential for the control system designer to ensure that the hydraulics within the column correspond to the design.

Over the years, there have been numerous books, articles and technical papers on techniques to achieve this objective. In particular, the work of F. G. Shinsky, **Figure 16**, and Foxboro has provided some excellent techniques for distillation control. In the experience of APV, the best technique for most systems is to control the reflux ratio by ratioing the distillate (product flow) to the returning reflux flowing from the reflux tank. This ensures that the top operating line on the McCabe-Thiele graph remains at a constant gradient. Thus the VLE conditions at the top of the column are as per design. To set the gradient of the bottom operating line, it is necessary to control the ratio of the energy input (usually steam flow rate to the reboiler) to the feed rate. Thus, all three flows into the column, namely vapor, reflux and feed, are flow controlled and in the correct ratio to each other. The bottom product flow is removed on the basis of bottom level control. With this technique, the necessary conditions to achieve the separation, combined with the theoretical plates provided, are in place. Now, the problem is to ensure that the mass balance is maintained.

For certain systems such as a steam stripper with top condensate phase separation, the mass balance controls itself, providing the energy input and feed flow rate are set up correctly. The overhead vapor is condensed to form two



*Figure 16. F.G. Shinsky book on distillation control.*



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phases which are decanted. The organic phase is pumped away under level control, and the aqueous phase is pumped under interface control back to the column as reflux. The water is pumped away under level control at the base of the column. In this application, the decanter controls the mass balance, and there is no need for additional control.

In the operation of a binary system, the steam to feed flow ratio control will only fulfill the hydraulics in the column. It will not control the mass balance. As there are variations in feed composition, the inventory of the two components in the system will change. For example, if the rate of removal of the more volatile component is lower than the feed rate of this component, it will build up in the column. The effect of this change will be an increase in the composition of this component in both the top product, which is acceptable, and in the bottom product, which is not acceptable. To prevent this from happening, it is necessary to adjust one or more of the following parameters: feed rate, energy input or reflux ratio. In the experience of APV, it is not good practice to change the energy input, and therefore the vapor loading, on an ongoing basis. This can cause the column to flood or dump and generally cause disturbances in the column. It is better to change the reflux ratio slightly or adjust the feed rate. Typically, if the feed composition is changing quite significantly, it is best to adjust the feed rate at constant energy input. However, if the feed composition is changing modestly, it is usually best to trim the reflux ratio within  $\pm 10\%$  levels.

The above techniques will ensure that a distillation column will operate in a stable manner. The major difficulty is determining the parameter on which the control should be based. Clearly, if an on-line analysis of the top and/or bottom product is available, or if other parameters such as density or refractive index can provide an accurate composition, the control is quite easy. With many distillation systems, however, on-line analysis is not very feasible, and the control has to be based on parameters other than composition. This is termed inferential control, which is an extremely common approach to distillation control. Here's the logic: providing the flows in the column are set up properly and the temperature is set at a given point in the column (usually around the mid-point) and is within a certain range, then the top and bottom product compositions must be at or better than design. This control system will usually work on simple and complex mixtures with varying feed compositions. If the actual components change, however, the control system needs to be recalibrated.

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Inferential control requires some excess theoretical plates so that the mass balance in the column can change without going off specification with the products. The mass balance change is usually sensed by temperature, with or without pressure compensation, at the point in the column where the temperature changes are at a maximum. This is generally at, or around the mid-point. It can also be close to the top or bottom when required product purities are quite low. The point chosen should not be within 1 or 2 theoretical plates of a feed point, due to possible temperature effects from a subcooled feed. When properly set up, the temperature profile of the column will remain steady except around the control point where there will be slight variation. This variation will indicate the precision of the control.

Most distillation systems are quite slow acting, particularly trayed columns where liquid hold up is high. This makes control somewhat easier for most applications.

## INSTRUMENTATION COMPONENTS

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Instrumentation components are similar to those used for most unit operations. Since most compounds distilled are volatile, flammable organics, it is necessary to use intrinsically safe loops or explosion proof equipment. A vapor pressure transmitter was one special instrument developed by Foxboro for distillation applications. This is an instrument used for the mass balance control point. The instrument essentially gives an inferred composition at a point in the column by measuring the offset between the vapor pressure of a product sample and the absolute pressure in the column. Today, with sophisticated PLC control, the same effect can be obtained with temperature and pressure transmitters and some software.

## CONTROL SYSTEM

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From a simple steam stripper that requires basic control of just two flows and one or two levels, to a complex multi-column system, there are many different control systems used to operate distillation systems. While many distillation systems can be controlled well with basic analog control loops, one advantage of accurate control is that there will be energy savings, due to the fact that there is no need to over concentrate the product to ensure that the product purity is always achieved. In addition, better control will usually enable the operator to increase the capacity of existing equipment. State-of-the-art systems, such as Connoisseur™ by Foxboro, are used to achieve this degree of control.

## M O D U L A R   S Y S T E M S

Many distillation systems are suitable for modular construction. The main advantage to modular construction is that most of the assembly of equipment and piping is carried out in the factory. This is far more efficient and generally much more economical than field construction. Also, this results in much shorter installation times on site.

For columns of 3 ft (900mm) diameter or smaller, it is usually possible to mount the column and all auxiliary equipment onto a single module. This can be shipped in one piece to site as shown in **Figure 17**. For larger columns, which have to be shipped separately and be freestanding, it is often possible to mount the auxiliary equipment, such as heat exchangers, small tanks and pumps, on a module. This is shown in **Figure 18** and **Figure 19**.

The main limitations on modular construction relate to shipping restrictions. Prior to detailing any modular design, it is essential to select the form of shipment and review the shipping limitations in all states and countries on the proposed route. Also, access to the proposed location at the plant must be studied together with reviewing any restrictions on offloading and rigging of the modules onto the foundations.



*Figure 17. Modular distillation system during transportation.*



*Figure 18. Petrojam where the 10 ft (3m) diameter column and reboiler are self standing.*



*Figure 19. Here the condenser, decanter and heat exchangers were assembled in the shop on three horizontal modules.*

Most systems are shipped by truck, which restricts the dimensions of the module and the weight. Rail transportation can, in some countries, allow for larger modules and is always preferable for particularly heavy equipment. This form of transportation, however, is significantly more expensive than trucking. If barge or ship transportation is possible, larger modules can be considered.

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# A P P L I C A T I O N S

## HIGH VACUUM DISTILLATION OF FLAVOR AND FRAGRANCE PRODUCTS

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There are many applications for distillation in the flavor industry. In particular, the separation of high boiling point oils is a key process in the purification of the flavor products. Typical components would be benzaldehyde, linalool, d-limonene, cinnamaldehyde and many other types of oils. These distillation systems are usually small batch columns which operate at high vacuum and high temperatures.

A typical system would utilize a batch still pot column with about 1,000 gallons (3.8m<sup>3</sup>) of capacity. In many cases, the system would have to process many different products and operate over a wide range of pressures and temperatures. Some systems supplied by APV have been designed to operate at pressures as low as 5mm Hg absolute and at temperatures up to 570°F (300°C). These conditions present significant challenges to both the process and mechanical designers.

To operate at these very low pressures, it is necessary to specify packing as the column internal, in order to minimize pressure drop. At APV, we have determined that corrugated gauze packing is preferred. This type of packing is particularly efficient at the low liquid loadings that occur during high vacuum distillation. APV systems have shown that it is feasible to achieve an HETP of 10 inches (250mm) with that style of packing. It is important to note that in order to achieve these high efficiencies, it is vital to have excellent liquid distribution at the top of the bed. The pressure drop characteristics of this style of packing are also exceptional.

The mechanical design presents an even more difficult challenge. To design a system for such high temperature, and at the same time maintain high levels of vacuum integrity, requires techniques significantly different from the norm. The major problem is coping with the expansion and contraction as the equipment is started up and shut down. These columns often are heated by reboilers using hot oil as the heating medium with temperatures up to 700°F (370°C). The final result is equipment that is designed and built to high mechanical standards. A typical system is shown during final assembly in the shop in **Figure 20**.





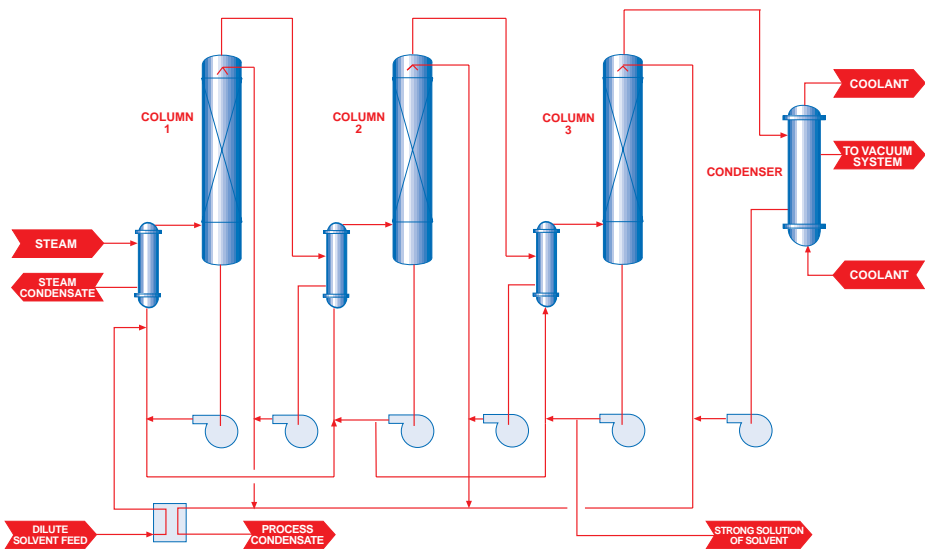
*Figure 20. Typical high vacuum distillation system under final shop assembly.*

## RECOVERY OF LOW VOLATILE SOLVENTS FROM WATER

Most solvents that are recovered from aqueous streams are more volatile than water, or form an azeotrope with water, so that the solvent can be distilled overhead. There are, however, a limited number of commonly used solvents that are less volatile than water. These include dimethylacetamide (DMAC), dimethylformamide (DMF), dimethylsulfoxide (DMSO), ethylene and propylene glycol. The recovery of these solvents from water streams is expensive since all the water has to be vaporized for removal. It is also necessary to have some water reflux, which further increases the energy consumption.

When the feed rate is high and the solvent concentration is low, the energy requirement is extremely high. The solvent recovery system must then be designed for energy recovery. The technique is to design a multi-effect distillation system. This is very similar to a multi-effect evaporator except for the presence of columns between each effect. A schematic of a typical system is shown in **Figure 21**.

In the system shown for the recovery of DMAC, the feed is preheated and fed to the first effect falling film calandria. A mixture of solvent and water is vaporized. This vapor is then rectified in the distillation column to enrich the water content. The vapor, which is predominantly water, is then condensed when it is



**Figure 21.** Multi-effect distillation.

used as the heating medium of the calandria of the next effect. The reflux ratio is adjusted to give the water purity required. The water product is removed from the system. A DMAC/water mixture is removed from the base of the column and pumped to the second effect, where the process is repeated at a lower pressure. The number of effects used is basically a function of steam costs and capacity, which can be as high as six.

As the solvent becomes progressively more concentrated, the temperature difference between the top and bottom of the column increases. Eventually it is necessary to use a separate medium pressure steam supply for the final DMAC purification. At that point, however, most of the water has been removed by the energy efficient multi-effect system.

When low volatiles such as oils or solids are present in the feed, it will be necessary to use an evaporator as the last stage to provide the solids-free solvent.

## AZEOTROPIC DISTILLATION

Many binary mixtures exhibit azeotropic behavior. That is, at a certain composition known as the azeotrope point, the vapor composition over the boiling liquid is exactly the same as the liquid. In other words, the azeotropic mixture of two or

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more components behaves, during the distillation process, the same as a pure component. As a result, simple distillation will not separate the components. A typical azeotrope is a 96% w/w mixture of ethanol in water.

To separate an azeotrope, it is necessary to change some conditions that will effect either relative volatilities or compositions. At APV, three different distillation techniques have been used to break azeotropic systems. Azeotropes also can be broken with membrane systems as well as molecular sieves. Membranes operating as pervaporation systems have found a limited number of applications for the removal of water from isopropyl alcohol, while molecular sieves have been used for the removal of water from ethanol/water mixtures.

### **Azeotropic Distillation With an Entraining Agent**

The most common form of azeotropic distillation is adding a third component to the azeotropic mixture in a distillation column. This third component essentially changes the vapor/liquid relationship between the two components and allows separation. Using ethanol/water as the example, the column is usually operated with a continuous feed of the azeotrope into the column, which contains the third component. This causes a ternary azeotrope to form in the vapor at the top of the column. When this vapor is condensed, the condensate splits into two liquid phases. The organic layer is pumped back to the top of the column as reflux. The aqueous layer is pumped to a smaller third column where the entrainer is recovered and pumped back to the dehydration column. Thus, the entrainer is continuously recycled and losses are low. In the base of the dehydration column, the entrainer is removed from the ethanol to give high purity ethanol as the base product. The process for the removal of water from the isopropyl alcohol/water azeotrope is essentially the same.

APV has supplied over 10 systems to remove water from both ethyl alcohol and isopropyl alcohol. Cyclohexane, isopropyl ether and benzene have been used as the entraining component. A large system for anhydrous ethyl alcohol production is shown in **Figure 22**.

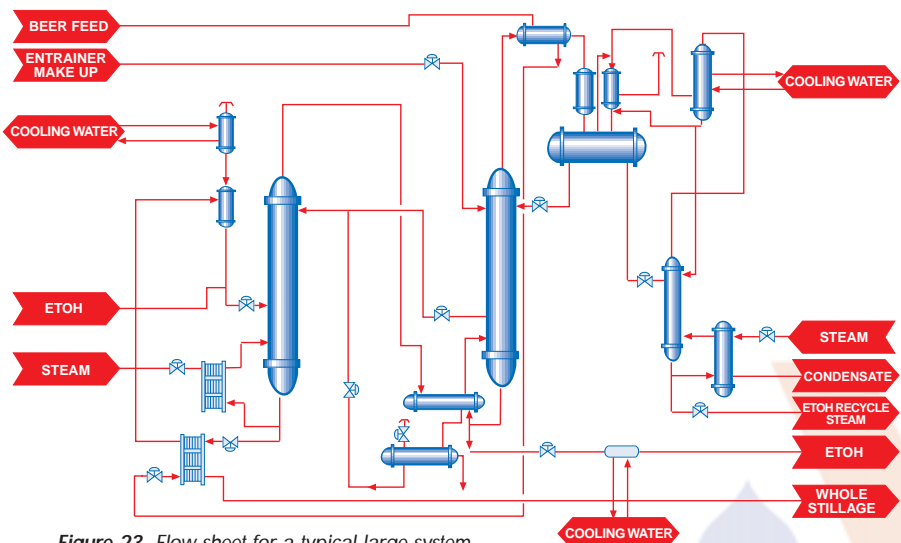
Many ethyl alcohol systems involve processing a feed of about 10% w/w ethyl alcohol. This is concentrated to 93% w/w in a binary column, followed by a concentration step to over 99% w/w in the azeotropic column. A flow sheet for a typical large system is shown in **Figure 23**. This system consists of a binary





*Figure 22. Large system for anhydrous ethyl alcohol production.*

column, dehydration column and entrainer recovery column. On these systems, the two larger columns are often operated at different pressures so that the vapor from one column can be used as the heating medium for the reboiler of the second column, which operates at a lower pressure. A column of the size illustrated above, in **Figure 22**, can process about 230,000 tons per year of ethyl alcohol.



*Figure 23. Flow sheet for a typical large system.*

## Azeotropic Distillation Without an Entraining Agent

Certain binary systems form vapor azeotropes that, when condensed, form a two phase liquid without the presence of a third component. The separation is achieved with the combination of an organic column and an aqueous column coupled with a decanter. This is shown schematically in **Figure 24**.

The vapors from each column are condensed, and the resulting two phase liquids are combined and decanted in a single vessel. The organic phase is returned as reflux to the organic column and the aqueous phase is returned as reflux to the aqueous column. The feed should enter the columns at a point that corresponds most closely to its composition. If the feed is at or close to the azeotrope, the feed point can be the decanter. In this process, the high purity products, which are usually water and organic, are removed from the base of the two columns.

APV has supplied this type of design for the dehydration of butyl alcohol and cyclohexanone.

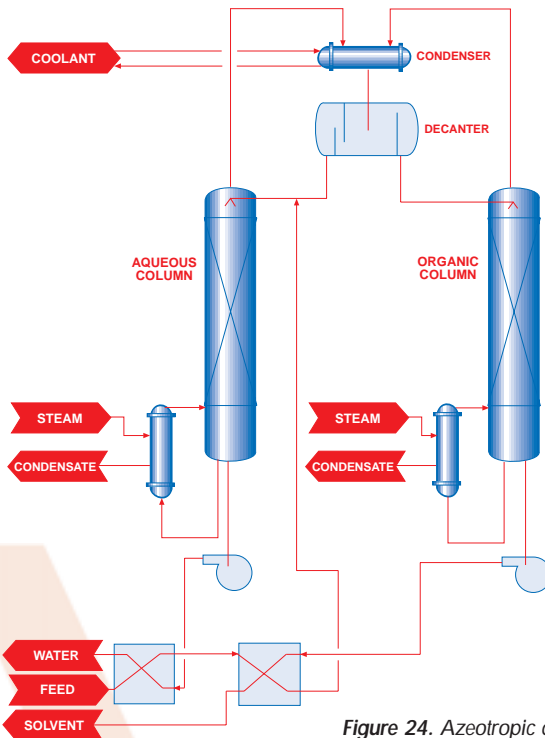


Figure 24. Azeotropic distillation with no entrainer.

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## Azeotropic Distillation Using Pressure Swings

Some azeotropic mixtures can be separated by changing the operating pressure of the column. This applies to those systems where the azeotropic composition is significantly affected by the operating pressure. APV has used this technique to separate the methyl ethyl ketone (MEK)/water system. In the process, the product is processed in the first column at atmospheric pressure to remove the azeotrope as a distillate. The azeotrope at 89% w/w is then pumped to a second column which operates at 74 psia (5 bar a). At this pressure, the azeotropic composition is at about 83% w/w, which is substantially lower than the feed composition. Therefore, it is possible to remove dehydrated MEK from the column bottom and take an azeotrope distillate at about 83% w/w from the top. This azeotrope is then recycled back to the first column. Since the columns are operated at different pressures and temperatures, it is possible to economize on energy by using vapor from the higher pressure column as the heat source for the lower pressure reboiler.



# C A S E S T U D Y

*Pharmacia & Upjohn Steam Stripper Case Study 1993*

*by Dr. Anthony Cooper, APV Americas*

In 1990, The Upjohn Company in Kalamazoo, Michigan, USA had a problem with the release of small quantities of methylene chloride into the atmosphere. The methylene chloride was actually in a waste water stream and was released during certain process operations on this water. Although the water contained other volatile organic chemicals, it was only necessary to design a process to remove the methylene chloride since other non-toxic organics would be processed downstream. In order to meet the regulations, a 99.99% removal of the methylene chloride was required.

	1. DESIGN INQUIRY		2. LABORATORY TEST PLANT	
COMPONENT:	Design Feed	Design Bottom	Lab Feed	Lab Bottom
Ethanol	200	124	200	72
Methanol	4400	1760	3800	2200
Methylene Chloride	11500	0.8	11500	< 0.5
Pyridine	Not Detected	Not Detected	Not Detected	Not Detected
Water	Balance	Balance	Balance	Balance

	3. INSTALLED COLUMN		4. COMPUTER SIMULATION OF INSTALLED COLUMN	
COMPONENT:	Actual Feed	Actual Bottom	UNIFAC Predicted	NRTL Predicted
Ethanol	5300	2700	1456	2456
Methanol	26000	18000	19205	19160
Methylene Chloride	13000	0.5	< 10 ppb	< 10 ppb
Pyridine	18	14	15	13
Water	Balance	Balance	Balance	Balance

*Figure 25. Comparison of actual laboratory and simulation data. Data shown in ppm.*

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APV had experience in the design of equipment to remove methylene chloride from water. A steam stripper already was in operation with a New Jersey operator where methylene chloride was removed from a waste water containing acetone. Test work and subsequent operating experience had shown that the presence of a fully water miscible compound, namely acetone, had a significant negative effect on the efficiency of the stripping of methylene chloride. With the Upjohn application, there were a number of fully miscible compounds present that would significantly affect the performance. These included methanol, ethanol, acetone, tetrahydrofuran and pyridine.

It was mutually agreed by both companies that, although the best technology available was steam stripping, the presence of so many compounds in the feed would make the design difficult. It was therefore decided to simulate the system using process simulation software. The design would be confirmed by test work on an actual plant sample. Two different thermodynamic equations, UNIQUAC and NRTL, were tried. Both were expected to give a reasonable correlation since all the necessary binary interaction parameters (BIPs), were known for the major components. The system was simulated to produce a bottom water product containing less than 1ppm of methylene chloride, which would provide the 99.99% recovery.

The data from the simulation was used in conjunction with some operating experience to predict the ratio of liquid to vapor (L/V) in the stripping section of the column and to estimate the required number of theoretical plates. This data was then used to build up the laboratory distillation column for test work with actual plant samples.

The laboratory column consisted of a vacuum jacketed 1<sup>1</sup>/<sub>4</sub> inch (30mm) diameter column with high efficiency metal gauze packing to provide the equivalent of 10 theoretical plates. Vapor was generated by a calibrated thermosiphon reboiler. A reflux splitter and positive displacement pumps provided flow measurements of liquid to and from the column. In addition, the mass balance was confirmed by collecting and weighing, over a specified time, the feed, overhead product and bottoms product.

The initial tests were unsuccessful and the 1ppm concentration could not be achieved at the 9:1 L/V ratio predicted. Even much lower ratios failed to achieve

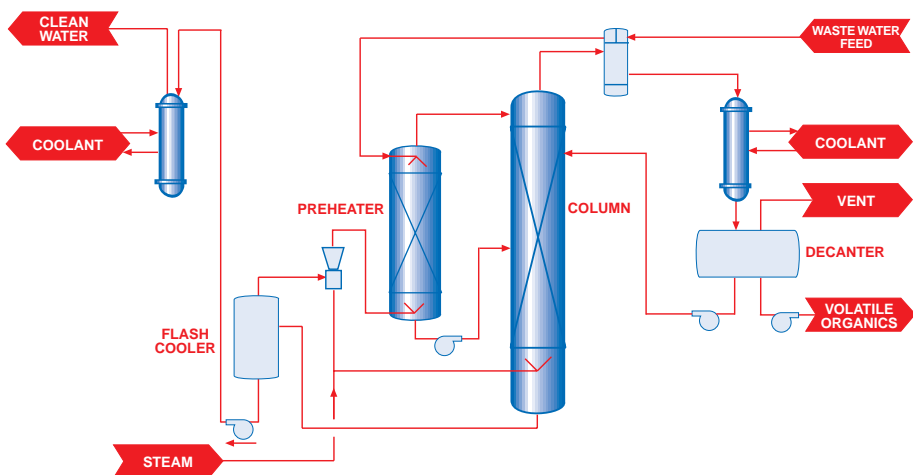
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the objective. An investigation of the feed, however, revealed significant concentrations of dimethylformamide (DMF), which had not been expected. This compound was probably acting as a strong co-solvent and dragging the methylene chloride down to the bottom. Since DMF was not expected to be normally in the feedstock, a further sample was obtained and a bottoms product of less than 0.5ppm was obtained. The initial design, with a few modifications, had been confirmed and the main parameters, namely theoretical plates and L/V ratio, had been established.

There still remained a number of other significant technical problems to be solved. In particular, the feed material was known to foul heat transfer surfaces at higher temperatures. Also, methylene chloride can hydrolyze at the operating conditions, produce hydrogen chloride in small quantities and provide serious corrosion problems. The corrosion problems were solved, albeit at high cost, by the specification of Hastelloy C-22 for equipment and PTFE lining for the piping. The fouling problem, however, presented a different challenge and was solved by incorporating direct contact heat transfer, as described later.

A further detail that had to be addressed was the design of the column overhead system. On many steam stripper systems where the volatile organic chemicals are only partially miscible in water, it is possible to decant the overhead condensate, return the aqueous phase as reflux and take off the organic phase as product. In this particular case, the presence of so many fully water miscible compounds meant that there would be the potential for a single phase overhead. This would prevent the decanter from operating. To reduce the amount of water in the overhead for all operating conditions, it was necessary to design a rectification system for the top of the column.

The final plant design is shown in **Figure 26**. Feed under flow control was pumped through the tube side of a shell and tube preheating condenser, where it extracted some of the heat from the overhead vapors. A further preheat occurred when the feed was sprayed into a direct contact condenser. This direct form of heating was specified to minimize the potential for fouling on heat transfer surfaces at the higher temperatures. The steam for preheating was supplied by flashing the bottom product and then using a steam jet compressor to boost the pressure to slightly in-excess of atmospheric pressure. The hot feed was then pumped to tray 18 in the distillation column. Trays were selected as internals for the column since



**Figure 26.** Flow schematic of the APV Americas steam stripper for the removal of 99.99% methylene chloride from a waste water stream.

the potential for fouling could have caused significant problems with packing internals. Vapor to the column was supplied by 150 psig (10 barg) steam before the control valve. These techniques enabled some heat to be recovered without the need to use heat transfer surfaces, which would foul and require frequent cleaning. In the column, the rising vapors stripped out the methylene chloride, which was further concentrated in the rectification section at the top of the column. The concentrated product was pumped away for methylene chloride recovery in a separate batch distillation column.

The system was small enough to be fully preassembled on a carbon steel structure in the factory prior to shipment.

After start up, a consulting company was assigned to test the system, and a significant amount of operational data was obtained. This has been compared with both laboratory and simulation data, and the results of one set of data are presented in Table 1. To make the comparison, the process simulation program was executed with the exact feed composition and operating conditions. The bottom product composition was compared with the actual. For comparison with

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the test work, the most similar test feed composition was used. As expected, the operating performance compared well with the laboratory test work and, therefore, the design. From the data, it would seem that the UNIFAC and NRTL models did not generate a good correlation, and a design based on the models would have been incorrect. In the case of NRTL, accurate data was expected since all 9 BIPs were established. While it may appear that the models are not correct, the most likely error in the calculations was probably in the conversion of the theoretical stage requirements into actual installed stages. This problem was reported in 1994 by FRI (1). Although there is still no complete explanation, it would appear that in the extremely low concentration range, the usual vapor diffusion limited mass transfer models are not controlling the transfer rate. The systems are liquid diffusion rate controlled. Very little data exists to validate predictive models. Test work was performed by FRI in a 4 ft. (1.2m) diameter column with sieve tray internals. This demonstrated that the overall tray efficiency on the toluene/water system at the ppm and ppb levels was typically in the range of 30–40%. Under normal conditions, a column of this diameter would give an efficiency in the range of 70–80%. When an overall tray efficiency of 30% is applied to this methylene chloride system, then the NRTL correlation predicts the methylene chloride stripping with tolerable accuracy. Unfortunately, the performance predictions for the other compounds not in the trace concentrations was inaccurate. Therefore, the separation efficiency for those compounds was higher.

The data from this commercial size system provides a revealing, but limited, insight into the problems of predicting stripping performance in the extremely low concentration range. Although the distillation process is old technology, it is only in recent years that this unit operation has been required to operate in such an extreme concentration range.



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*The author acknowledges the Upjohn Company for their approval in the publication of this article.*

**Reference**

*1 J.G. Kunes, T.P. Ognisty, M. Sagata, G.X. Chen, AIChE, Spring National Meeting, 1994, Atlanta.*



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## MAJOR APV DISTILLATION CUSTOMERS

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- SmithKline Beecham . . . . .USA/UK/Ireland
- Eli Lilly . . . . .USA
- BASF . . . . .USA
- Pharmacia & Upjohn . . . . .USA
- Pfizer . . . . .USA/Puerto Rico/UK
- Abbott Laboratories . . . . .USA/Puerto Rico
- Monsanto . . . . .USA
- Polfa . . . . .Poland
- Union Texas Petroleum . . . . .USA
- SAV . . . . .France
- Anheuser Busch . . . . .USA
- IBM . . . . .USA/Canada
- Syntex . . . . .USA
- Polaroid . . . . .USA
- W.R. Grace . . . . .USA
- Cyanamid . . . . .USA
- Coca Cola . . . . .USA
- Goodyear . . . . .USA
- Bristol-Meyers Squibb . . . . .USA/Puerto Rico
- Fresenius . . . . .USA
- Merck . . . . .USA
- Unocal . . . . .USA
- Sartomer . . . . .USA
- Witco . . . . .USA
- Olin . . . . .USA

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- Ciba Geigy . . . . .USA
  - Union Carbide . . . . .USA
  - Formosa Chemical . . . . .Taiwan
  - Hercules . . . . .USA
  - IFF . . . . .USA
  - Staley . . . . .USA
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  - Tandy . . . . .USA
  - General Electric . . . . .USA
  - Rockwell . . . . .USA
  - Jefferson Smurfit . . . . .USA
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  - Biocraft . . . . .USA
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  - Rodel . . . . .USA
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  - National Starch . . . . .USA
  - Vulcan Chemical . . . . .USA
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