

## MURPHREE EFFICIENCY IN DISTILLATION BY McCABE THIELE METHOD

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### ABSTRACT

Distillation is a unit operation which involves separation of a vaporizable component from a multi-component system and subsequent condensation of vapours. The pressure exerted by the vapor at the equilibrium state is termed as the vapor pressure of the liquid. The opposite process of this vaporization is called condensation. At equilibrium, the rates of these two processes are same. In order to model the vapor temperature, the Murphree efficiency equation is used to calculate the change of vapor temperature between vapor inlet temperature and liquid outlet temperature, which will only be reached at full efficiency. As a result, vapor temperature will be much nearer to its dew point, which better matches reality.

**KEYWORDS:** Distillation, theoretical plates, McCabe Thiele method, vapour pressure, equilibrium.

### INTRODUCTION

Continuous distillation, a form of distillation, is an ongoing separation in which a mixture is continuously (without interruption) fed into the process and separated fractions are removed continuously as output streams. Distillation is the separation or partial separation of a liquid feed mixture into components or fractions by selective boiling (or evaporation) and condensation. The process produces at least two output fractions. These fractions include at least one volatile distillate fraction, which has boiled and been separately captured as a vapor condensed to a liquid, and practically always a bottoms (or residuum) fraction, which is the least volatile residue that has not been separately captured as a condensed vapor. An alternative to continuous distillation is batch distillation, where the mixture is added to the unit at the start of the distillation, distillate fractions are taken out sequentially in time (one after another) during the distillation, and the remaining bottoms fraction is removed at the end. Because each of the distillate fractions are taken out at different times, only one distillate exit point (location) is needed for a batch distillation and the distillate can just be switched to a different receiver, a fraction-collecting container. Batch distillation is often used when smaller quantities are distilled. In a continuous distillation, each of the fraction streams is taken simultaneously throughout operation; therefore, a separate exit point is needed for each fraction. In practice when there are multiple distillate

fractions, the distillate exit points are located at different heights on a fractionating column. The bottoms fraction can be taken from the bottom of the distillation column or unit, but is often taken from a reboiler connected to the bottom of the column. Each fraction may contain one or more components (types of chemical compounds). When distilling crude oil or a similar feedstock, each fraction contains many components of similar volatility and other properties. Although it is possible to run a small-scale or laboratory continuous distillation, most often continuous distillation is used in a large-scale industrial process. Stage wise operations for gas/liquid contact, such as absorption, desorption and distillations are carried out in trayed columns. The column diameter, tray spacing, and the number of actual trays are the most important parameters for tray column design. Column diameter and tray spacing largely depend upon gas flow rate and total column pressure; these parameters can be estimated with great accuracy. The most difficult problem in column design is estimating the actual number of trays. The simple empirical method for estimating the actual number of trays is to divide the required number of theoretical stages by the overall tray efficiency.<sup>[1]</sup>

$$N_o = [N_t/E_o] \times N_0$$

A theoretical stage is defined as one in which the effluent phases are in equilibrium, so that a longer contact time will bring no additional change in composition. Another

method for tray number estimation is based on Murphree tray-efficiency prediction for each tray. This method can be used to calculate the actual number of trays. The definition of overall efficiency strictly applies only when the Murphree tray efficiencies of all trays are the same and when the equilibrium and operating lines are both straight over the concentrations considered. However, it is more accurate to determine the actual number of trays using the procedure based on Murphree tray efficiencies (from tray to tray), especially for systems where the slope of the equilibrium line significantly changes with the liquid-phase concentration.<sup>[2]</sup>

#### In general the efficiency depends upon:

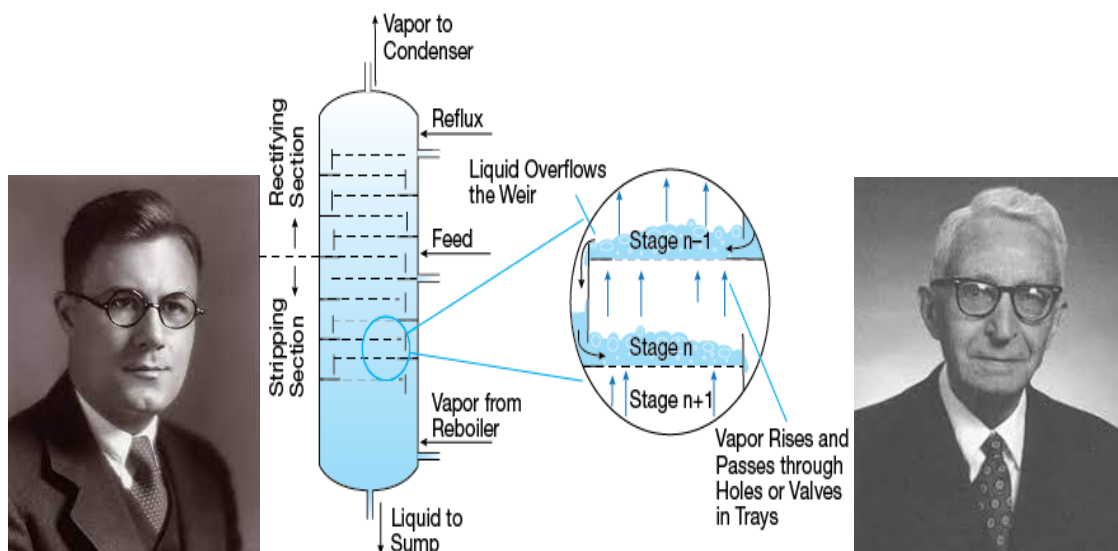
1. Tray variables (geometrical characteristics) such as column diameter, average flow width, length of liquid travel, bubbling area
2. Gas and liquid volumetric flow rate
3. Gas and liquid density
4. Gas and liquid viscosity
5. Gas and liquid diffusivity
6. Stripping factor

In a distillation column liquid and vapour are contacted while passing over and through trays (sometimes referred to as plates). In a theoretical analysis of the column performance such as the McCabe-Thiele method, the trays are assumed to operate at maximum efficiency. This means that the vapour and liquid phases are assumed to reach equilibrium as they interact over the plate. However, in practice there are many reasons why the vapour and liquid phases will not reach equilibrium as they pass.<sup>[3]</sup>

**The McCabe-Thiele Method:** This method uses the equilibrium curve diagram to determine the **number of theoretical stages (trays)** required to **achieve a desired degree of separation**. The **McCabe-Thiele method** is a chemical engineering technique for the analysis of binary distillation. It uses the fact that the composition at each theoretical tray (or equilibrium stage) is completely determined by the mole fraction of one of the two components and is based on the assumption of constant molar overflow, which requires that:

- The molar heats of vaporization of the feed components are equal;
- For every mole of liquid vaporized, a mole of vapor is condensed; and
- Heat effects such as heat of solution are negligible.

The method was first published by **Warren L. McCabe** [Warren Lee McCabe (August 7, 1899 – August 24, 1982) was an American Physical Chemist and is considered as one of the founding fathers of the profession of chemical engineering. He is widely known for the eponymous McCabe-Thiele method for analysis of distillation processes and his book, Unit Operations of Chemical Engineering, a major textbook.] and **Ernest Thiele** [Ernest W. Thiele (1895–1993) was an influential chemical engineering researcher at Standard Oil (then Amoco, now BP) and Professor of Chemical Engineering at the University of Notre Dame. He is known for his highly impactful work in chemical reaction engineering, complex reacting systems, and separations, including distillation theory] in 1925, both of whom were working at the Massachusetts Institute of Technology (MIT) at the time.<sup>[4]</sup>



**Figure-1: Distillation takes place in a column with crossflow trays over which liquid flows in alternate directions on successive trays. The topmost tray has the highest concentration of the more volatile species and the lowest tray has the highest concentration of the less volatile species [Left: Warren L. McCabe & Right: Ernest Thiele].**

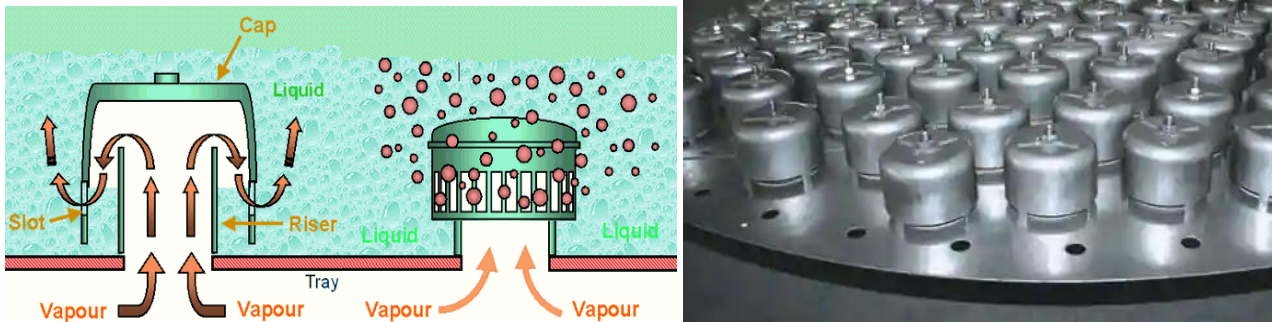


Figure 2: Typical bubble cap trays used in industrial distillation column.



Figure 3: Continuous Distillation unit (Left: Industrial Basis, Middle: Laboratory Basis, Right: Diagram).

**Construction**

A McCabe–Thiele diagram for the distillation of a binary feed is constructed using the vapor-liquid equilibrium (VLE) data for the lower-boiling component of the feed.<sup>[5]</sup>

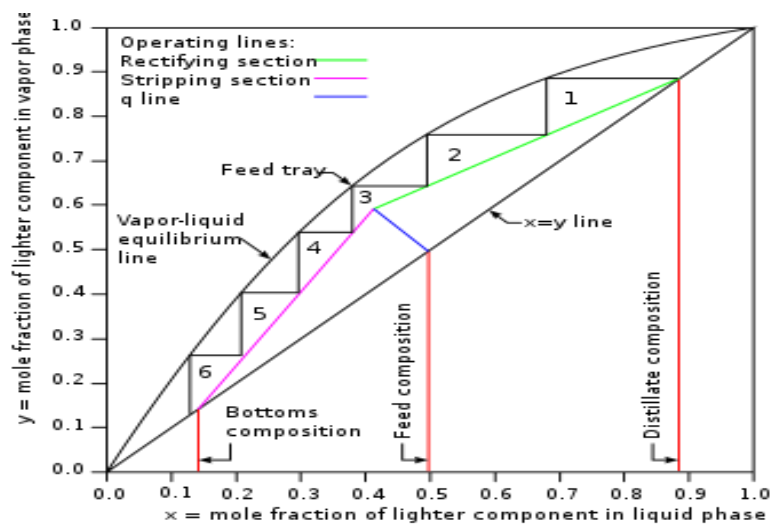


Figure 4: Typical McCabe–Thiele diagram for distillation of a binary feed.

On a planar graph with the horizontal (x) axis representing the mole fraction of the lower-boiling feed component in the liquid phase and the vertical (y) axis representing the mole fraction of the lower-boiling feed component in the vapor phase, the 45-degree  $x = y$  line

(Figure 4) is used as a graphical aid. The equilibrium line (black line in Figure 4), drawn using the VLE data points of the lower boiling component, represents the equilibrium vapor phase compositions for each value of liquid phase composition. Vertical lines from the

horizontal axis up to the  $x = y$  line indicate the feed and desired compositions of the top distillate product and the corresponding bottoms product (shown in red in Figure 4).

The rectifying section operating line for the section above the feed inlet of the distillation column (shown in

green in Figure 4) starts at the intersection of the distillate composition line and the  $x = y$  line and continues at a downward slope ( $\Delta y/\Delta x$ ) of  $L / (D + L)$ , where  $L$  is the molar flow rate of reflux and  $D$  is the molar flow rate of the distillate product.<sup>[6]</sup>

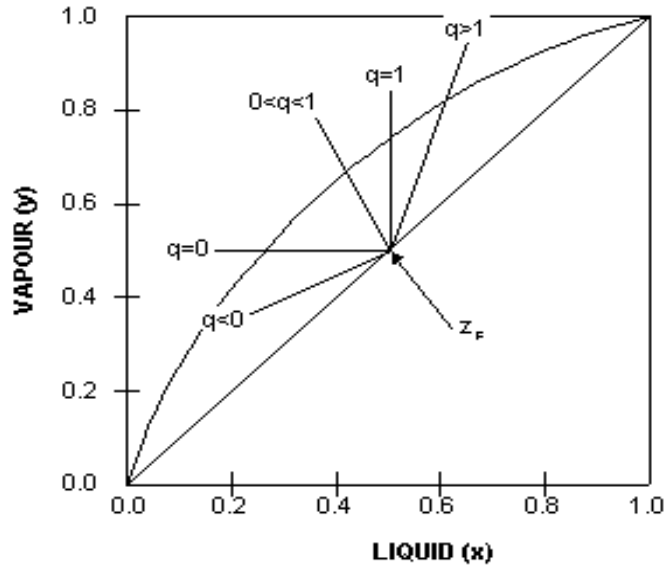
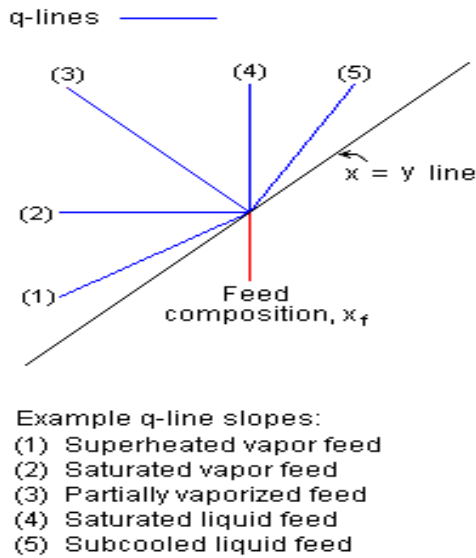


Figure-5: Examples of q-line slopes.

The q-line (depicted in blue in Figure 1) starts at the  $x = y$  line and intersects the starting point of the rectifying section operating line. The parameter  $q$  is the mole fraction of liquid in the feed, and the slope of the q-line is  $q / (q - 1)$ . For example, if the feed is a saturated liquid, it has no vapor, thus  $q = 1$  and the slope of the

q-line is infinite (a vertical line). As another example, if the feed is all saturated vapor,  $q = 0$  and the slope of the q-line is 0 (a horizontal line). The typical McCabe-Thiele diagram in Figure 1 uses a q-line representing a partially vaporized feed. Example q-line slopes are presented in Figure 5.<sup>[7]</sup>

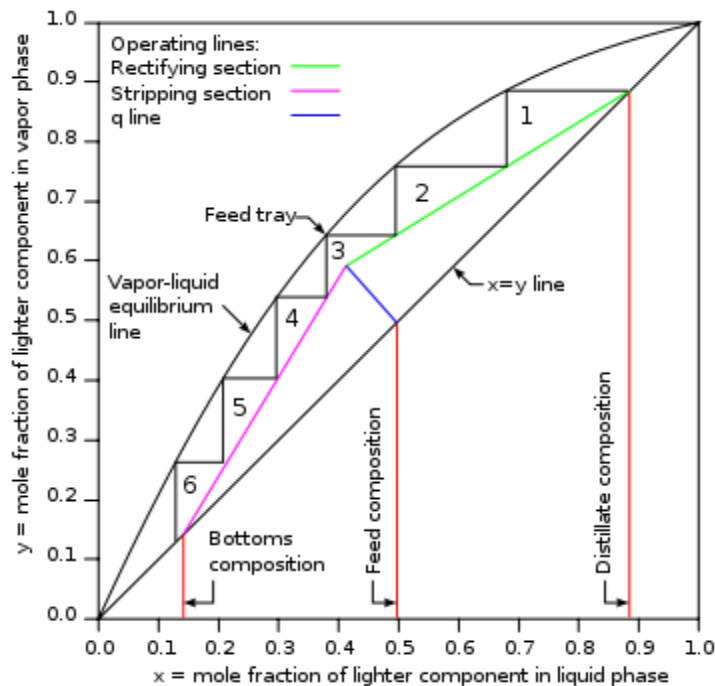


Figure-6: McCabe-Thiele Diagram for Murphree Efficiency.

The stripping section operating line for the section below the feed inlet (shown in purple in Figure 4) starts at the intersection of the red bottoms composition line and the  $x = y$  line and continues up to the point where the blue  $q$ -line intersects the green rectifying section operating line. The number of steps between the operating lines and the equilibrium line represents the number of theoretical plates (or equilibrium stages) required for the distillation. For the binary distillation depicted in Figure 4, the required number of theoretical plates is 6.<sup>[8]</sup>

Constructing a McCabe–Thiele diagram is not always straightforward. In continuous distillation with a varying reflux ratio, the mole fraction of the lighter component in the top part of the distillation column will decrease as the reflux ratio decreases. Each new reflux ratio will alter the slope of the rectifying section operating line. When the assumption of constant molar overflow is not valid, the operating lines will not be straight. If the mixture can form an azeotrope, its vapor-liquid equilibrium line will cross the  $x = y$  line, preventing further separation no matter the number of theoretical plates.<sup>[9]</sup>

#### Limitations of McCabe Thiele Method for Distillation

- It is not used when relative volatility is less than 1.3 or greater than 5.
- It is not used when more than 25 theoretical stages/plates are required
- It is not used when the operating reflux ratio is less than 1.1 times the minimum reflux ratio.

**Tray Efficiency:** Tray efficiency in general is considered to be a measure of the degree of approach to an ideal tray – an ideal or equilibrium tray being defined as one on which both the vapor and liquid phases leaving the tray are in mutual thermodynamic equilibrium. For the analysis of theoretical stage required for the distillation, it is assumed that the vapor leaving each tray is in equilibrium with the liquid leaving the same tray and the trays are operating at 100% efficiency. In practice, the trays are not perfect. There are deviations from ideal conditions. The equilibrium with temperature is sometimes reasonable for exothermic chemical reaction but the equilibrium with respect to mass transfer is not often valid. The deviation from the ideal condition is due to: (1) Insufficient time of contact (2) Insufficient degree of mixing. To achieve the same degree of desired separation, more trays will have to be added to compensate for the lack of perfect separability. The concept of tray efficiency may be used to adjust the the actual number of trays required.

#### Overall Efficiency

**The overall tray efficiency, EO is defined as**

$$E_o = (\text{Number of theoretical trays}) / (\text{number of actual trays})$$

It is applied for the whole column. Every tray is assumed to have the same efficiency. The overall efficiency depends on the (i) geometry and design of the contacting

trays, (ii) flow rates and flow paths of vapor and liquid streams, (iii) Compositions and properties of vapor and liquid streams.

**Murphree Efficiency:** The Murphree plate efficiency is therefore expressed as the ratio of the increase in mole fraction of vapour of a volatile component passing through a plate in a column to the same increase when the vapour is in equilibrium. In effect, more stages are therefore required to bring about a desired separation. The efficiency of the tray can also be calculated based on semi-theoretical models which can be interpreted by the Murphree Tray Efficiency EM. In this case it is assumed that the vapor and liquid between trays are well-mixed and have uniform composition. It is defined for each tray according to the separation achieved on each tray based on either the liquid phase or the vapor phase. For a given component it is equal to the change in actual concentration in the phase, divided by the change predicted by equilibrium condition. These definitions of Murphree tray efficiency are for the overall tray and involve the average vapor and liquid composition leaving the tray, this means that both the liquid and vapor leaving a given tray are assumed to be completely mixed and as a consequence no concentration gradient exists cross the tray. The assumption of complete mixing is unrealistic except for special cases in very small columns. Incomplete liquid mixing and vapor channeling are two common conditions which will result in deviations from Murphree's assumption.

The Murphree point vapor efficiency describes the degree of approach to equilibrium between the vapor and liquid at a single point on a tray. The plate efficiency is lower in the columns operated at high velocity because of significant entrainment.<sup>[10]</sup>

#### The traditional Murphree efficiency approach to tray design

The section efficiency is calculated based on fundamental mass-transfer considerations, including the approach to equilibrium both locally on the tray (point efficiency) and on the tray as a whole (tray efficiency). The conventional method of designing trays employs Murphree's definition of efficiency to quantify the approach to equilibrium. The overall number of transfer units for the gas phase ( $N_{OG}$ ) is (1):

$$(N_{OG})^{-1} = [(N_G)^{-1} + \lambda(N_L)^{-1}]$$

where  $N_G$  and  $N_L$  represent the number of transfer units in the gas and liquid phases (a measure to quantify mass transfer), respectively, and  $\lambda$  is the stripping factor calculated as  $\lambda = mG/L$ , where  $m$  is the slope of the equilibrium line and  $G$  and  $L$  are the gas and liquid flow rates per cross-sectional bubbling area in  $\text{kmol/m}^2/\text{s}$ .

The approach to equilibrium that can be achieved with a given number of transfer units depends on the concentration profile — the driving force for mass transfer, which, in turn, depends on the flow pattern of

the vapor and liquid phases. Most models for crossflow trays assume that the vapor flows vertically in plug flow and the liquid is vertically well mixed. With these assumptions, the Murphree point efficiency on a tray is defined as (1).

The Murphree vapor-phase tray efficiency ( $\eta_{tray}$ ) defines the fractional approach to equilibrium for a single crossflow tray based on the vapor concentrations on the operating and equilibrium lines. When the equilibrium line is steeper than the operating line, as is typically the case for the stripping section of a column, the stripping factor is greater than one and the section efficiency is less than the tray efficiency. When the stripping factor is less than one, the section efficiency is higher than the tray efficiency, which typically occurs in the rectifying section. When the stripping factor is exactly one the section and tray efficiencies are equal.

### LIMITATIONS

Several limitations of the Murphree efficiencies have been discussed by Standard. Murphree efficiencies are concerned only with mass transfer on the tray and ignore the transfer of heat. Constant molal flow rates along the column were assumed when Murphree defined the efficiencies and application includes this assumption since the variable is mole fraction of each component and not total moles of each component. The vapor and liquid efficiencies are related but not equivalent.<sup>[11]</sup>

### CONCLUSIONS

The concept of theoretical plates in designing distillation processes has been discussed in many reference texts. Any physical device that provides good contact between the vapor and liquid phases present in industrial scale distillation columns or laboratory scale glassware distillation columns constitutes a "plate" or "tray". Since an actual, physical plate can never be a 100% efficient equilibrium stage, the number of actual plates is more than the required theoretical plates. Where the number of actual, physical plates or trays is, is the number of theoretical plates or trays and is the plate or tray efficiency. So-called bubble cap or valve cap trays are examples of the vapor and liquid contact devices used in industrial distillation columns. Another example of vapor and liquid contact devices are the spikes in laboratory Vigreux fractionating columns. The trays or plates used in industrial distillation columns are fabricated of circular steel plates and usually installed inside the column at intervals of about 60 to 75 cm (24 to 30 inches) up the height of the column. That spacing is chosen primarily for ease of installation and ease of access for future repair or maintenance.

An example of a very simple tray is a perforated tray. The desired contacting between vapor and liquid occurs as the vapor, flowing upwards through the perforations, comes into contact with the liquid flowing downwards through the perforations. In current modern practice, as

shown in the adjacent diagram, better contacting is achieved by installing bubble-caps or valve caps at each perforation to promote the formation of vapor bubbles flowing through a thin layer of liquid maintained by a weir on each tray. To design a distillation unit or a similar chemical process, the number of theoretical trays or plates (that is, hypothetical equilibrium stages),  $N_t$ , required in the process should be determined, taking into account a likely range of feedstock composition and the desired degree of separation of the components in the output fractions. In industrial continuous fractionating columns,  $N_t$  is determined by starting at either the top or bottom of the column and calculating material balances, heat balances and equilibrium flash vaporizations for each of the succession of equilibrium stages until the desired end product composition is achieved. The calculation process requires the availability of a great deal of vapor-liquid equilibrium data for the components present in the distillation feed, and the calculation procedure is very complex.

In an industrial distillation column, the  $N_t$  required to achieve a given separation also depends upon the amount of reflux used. Using more reflux decreases the number of plates required and using less reflux increases the number of plates required. Hence, the calculation of  $N_t$  is usually repeated at various reflux rates.  $N_t$  is then divided by the tray efficiency,  $E$ , to determine the actual number of trays or physical plates,  $N_a$ , needed in the separating column. The final design choice of the number of trays to be installed in an industrial distillation column is then selected based upon an economic balance between the cost of additional trays and the cost of using a higher reflux rate.

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