

Optimal distillation using thermodynamic geometry

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Abstract

The thermal efficiency of a distillation column may be improved by permitting heat exchange on every tray rather than only in the reboiler and the condenser. Thermodynamic length optimizations on discrete systems specify the optimal temperature of each tray and consequently the amount of heat to be added or withdrawn in order to maintain that temperature.

1. Introduction

Geometric aspects have always played a prominent role in FTT optimizations. One of the early results [1] is a general bound on the entropy produced in bringing a thermodynamic system from a given initial to a given final state through a sequence of steps. The system is required to follow a prescribed equilibrium path specified by N intermediate equilibrations with the environment. For an arbitrary sequence of reservoirs this bound provides the lower limit on the entropy generated by this process. The derivation also shows how these N intermediate reservoirs may guide the system in the least dissipative fashion from the initial to the final state. Such a process has become known as a *horse-carrot process* and the associated bound as the *horse-carrot theorem* since the system (the ‘horse’) is coaxed along a sequence of states by successive contacts with generalized baths (the ‘carrots’). The intensities of these baths (temperature, pressure, etc.) define successive states in a sequence of equilibria.

Fractional distillation [2] is a very old process used to separate a mixture of compounds into its components of specified purity by making use of differences in boiling point. The liquid and vapor phases of the mixture are brought into equilibrium with one another at successive points along a column which is heated at the bottom and cooled at the top. In trayed columns these equilibrations occur on the trays, i.e. at a finite number of discrete points, while packed columns provide continuous contact between liquid and vapor. In this gradient of temperature, the more volatile components will preferentially migrate to the top of the column and the less volatile components to the bottom. In the remainder of this paper we

consider only binary separation for simplicity and trayed columns for their correspondence to the step processes mentioned above.

It is the goal of this paper to extend the general results for step processes to the steady state separation inside a distillation column in order to minimize the entropy production. In section 2 below, we define the thermodynamic geometry. Section 3 derives the optimal path for a staged process. Section 4 provides some comments on traditional distillation as a prelude to finding the optimal interior temperature profile of the column. This profile is obtained by geometric means in Section 5. Finally section 6 contains an example of the savings which are possible with this new temperature profile.

2. Thermodynamic length

Thermodynamic geometry lives in the space of all the extensive thermodynamic variables of a system: energy, entropy, volume, amount of material 1, amount of material 2, etc. In this space Weinhold [3, 4] defined a metric which is the second derivative of one extensive quantity (usually entropy or energy) with respect to the other extensive quantities. For example, in the energy picture, the system is described by the internal energy $U(S, V, N_1, N_2, \dots)$ expressed in terms of the other extensive quantities. The metric in this picture is

$$\mathbf{M}_U = \left\{ \frac{\partial^2 U}{\partial X_i \partial X_j} \right\} \quad (1)$$

with the remainder of the extensive variables represented by X_i . Weinhold's purpose was the calculation of all the usual partial derivatives in traditional static thermodynamics at a particular point. However, any metric invites integration over a range of its variables, in this case leading to the definition of a thermodynamic length L [5] by the usual formula

$$L_U = \int dL_U = \int \sqrt{d\mathbf{X} \mathbf{M}_U d\mathbf{X}}. \quad (2)$$

Boldface indicates vector quantities. The alternative mixed form of the differential length

$$dL_U = \sqrt{d\mathbf{Y} d\mathbf{X}}, \quad (3)$$

where $\mathbf{Y} = \partial U / \partial \mathbf{X}$ is the vector of intensive quantities conjugate to \mathbf{X} , may be useful if some of those elements happen to be constant, e.g. temperature or pressure.

Salamon and Berry [6] found a connection between this thermodynamic length along a continuous process path and the (reversible) availability lost in the process. Specifically, if the system moves via states of local thermodynamic

equilibrium from an initial equilibrium state i to a final equilibrium state f in time τ , then the dissipated availability $-\Delta A$ is bounded from below by the square of the distance (i.e. length of the shortest path) from i to f times ϵ/τ , where ϵ is a mean relaxation time of the system. If the system proceeds entirely through a sequence of equilibrium states the bound can be strengthened to

$$-\Delta A \geq \frac{L_U^2 \epsilon}{\tau}, \quad (4)$$

where L_U is the length of the *traversed* path from i to f . This will be the case for example if the process is endoreversible, i.e. the system is reversible in its interior while all irreversibilities are associated with its coupling to the environment [7]. Equality in eq. (4) is achieved at constant thermodynamic speed $v = dL/dt$, assuming that the process proceeds slowly, i.e. is close to equilibrium with the environment at all times. At higher speeds corrections may be applied [8].

Viewed in the entropy picture $S(U, V, N_1, N_2, \dots)$ an analogous expression exists for the total entropy production during the process:

$$\Delta S^u \geq \frac{L_S^2 \epsilon}{\tau}, \quad (5)$$

where the length L_S is then calculated relative to the entropy metric

$$\mathbf{M}_S = - \left\{ \frac{\partial^2 S}{\partial X_i \partial X_j} \right\}. \quad (6)$$

When expressed in identical coordinates these two metrics are related by [9] $\mathbf{M}_U = -T \mathbf{M}_S$, where T is the temperature of the system.

3. Optimization of a step process

First consider a single step [1] where a system described by the extensive variables X_i is coming to equilibrium with an environment at the intensities Y_i^0 , the simplest possible horse-carrot process. The system intensities conjugate to X_i will, in the entropy picture, be denoted by $Y_i = \partial S / \partial X_i$. Specifically $\mathbf{X} = (U, V, N, \dots)$ and $\mathbf{Y} = (1/T, -p/T, \mu/T, \dots)$. Then a second order power series expansion of the system entropy S about equilibrium yields

$$S = S^0 + \sum_i Y_i^0 (X_i - X_i^0) - \frac{1}{2} \sum_{ij} (X_i - X_i^0) M_{ij}^0 (X_j - X_j^0), \quad (7)$$

where the superscript zero denotes values at equilibrium with the environment. Then the change in entropy of the system becomes

$$\Delta S = S^0 - S = - \sum_i Y_i^0 \Delta X_i + \frac{1}{2} \sum_{ij} \Delta X_i M_{ij}^0 \Delta X_j. \quad (8)$$

The corresponding change of entropy of the environment (reservoir) is

$$\Delta S^{\text{en}} = - \sum_i Y_i^{\text{en}} \Delta X_i^{\text{en}}, \quad (9)$$

since its intensive quantities Y_i^{en} are constant. At equilibrium $Y_i^0 = Y_i^{\text{en}}$, and conservation of energy and matter relates $\Delta X_i = -\Delta X_i^{\text{en}}$, yielding a total change of entropy of the universe as a result of this small equilibration process

$$\Delta S^{\text{u}} = \Delta S + \Delta S^{\text{en}} = \frac{1}{2} \sum_{ij} \Delta X_i M_{ij}^0 \Delta X_j \quad (10)$$

or in matrix notation

$$\Delta S^{\text{u}} = \frac{1}{2} \Delta \mathbf{X} \mathbf{M} \Delta \mathbf{X}. \quad (11)$$

The superscript zero on \mathbf{M} indicating an equilibrium value will be presupposed in the following.

Next consider N consecutive small steps. The n th step in this sequence produces the dissipation

$$\Delta S^{\text{u}n} = \frac{1}{2} (D_S^n)^2, \quad (12)$$

where

$$D_S^n = \sqrt{\Delta \mathbf{X}^n \mathbf{M}_S^n \Delta \mathbf{X}^n} \quad (13)$$

to first order in the stepsize is the thermodynamic length of the step. Summing over all N steps in the process, we find using the Cauchy-Schwarz inequality

$$\Delta S^{\text{u}} = \frac{1}{2} \sum_{n=1}^N (D_S^n)^2 \geq \frac{1}{2N} \left(\sum_{n=1}^N D_S^n \right)^2 = \frac{L_S^2}{2N}, \quad (14)$$

where $L_S = \sum D_S^n$ is the thermodynamic length of the full N -step process. Similar to the continuous results eqs. (4) and (5), equality is achieved only when all D_S^n are equal.

This bound and the optimal equality of all steps (in thermodynamic geometry), valid for many small steps, are the crucial results used in the following analysis of the distillation process.

4. A classical distillation column

A conventional binary distillation column is constructed as sketched in Fig. 1 with feed entering at the steady state rate F around the middle of the column and being separated into distillate leaving the top at rate D and waste W (also called bottoms) leaving at the bottom. The mole fractions x_F , x_D , and x_W refer to the light component in those three streams. The separation is affected by a heat flow q_W entering the bottom at temperature T_W and a corresponding flow q_D leaving the top at the lower temperature T_D , thus creating vapor flows V and liquid flows L inside the column. In all large scale distillation columns interior equilibration between vapor and liquid is achieved on trays where vapor bubbles through a thin layer of liquid.

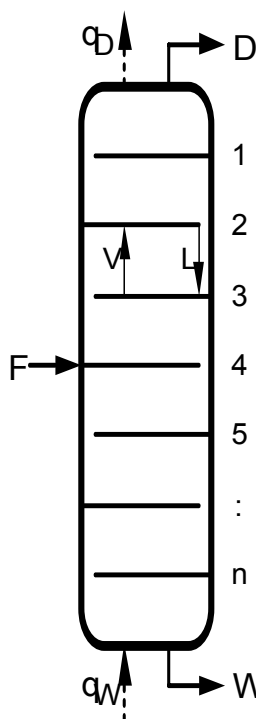


Figure 1. Sketch of a conventional distillation column with feed, distillate, and waste (bottoms) rates F , D , W , heating and cooling rates q_W and q_D , and tray numbers n .

The reversible separation (unmixing) of a feed stream F into its pure components ($x_D = 1$, $x_W = 0$) requires the power [2]

$$W_{\text{rev}} = -RT_D [x_F \ln x_F + (1-x_F) \ln(1-x_F)] F, \quad (15)$$

where R is the gas constant. Mass and energy conservation inside a conventional distillation column, on the other hand, requires a minimum heat flow

$$q_{\min} = FR \frac{T_D T_W}{T_W - T_D} \quad (16)$$

as derived in any chemical engineering text book [2]. Using the Carnot efficiency, this is equivalent to a theoretical power

$$W_{\min} = \frac{T_W - T_D}{T_W} q_{\min} = FRT_D. \quad (17)$$

Thus the thermal efficiency of a distillation column can never exceed

$$\varepsilon = W_{\text{rev}}/W_{\min} = - [x_F \ln x_F + (1-x_F) \ln(1-x_F)] \quad (18)$$

which has a maximum of $\ln 2$, about 70%, for an equal mixture feed, $x_F=0.5$. Deviation from this balanced feed as well as any non-idealities in the system will further reduce the efficiency. Considering that distillation consumes a sizable fraction of the world energy demand, this is an unfortunate situation. Of course, a completely equivalent analysis can be carried out in terms of entropy produced during the separation.

The internal distribution of temperature and mole fractions of light and heavy components in a conventional distillation column where heat is added and withdrawn only in the reboiler and the condenser, respectively, is fixed exclusively by the conservation laws for energy and mass. In most long columns this leads to an S-shaped curve of composition versus tray number with most of the variation occurring near the end points of the column, connected with a flat stretch around the feed point (see Fig. 2). A qualitatively similar picture emerges for the temperature. This composition profile implies that the major part of the entropy production in the distillation process occurs near the ends of the column and is thus not uniformly distributed. Even more importantly, if the number of trays is increased, essentially only the middle flat section is extended while the segments of rapid variation are unchanged. This means that dissipation does not approach zero as the number of trays goes to infinity.

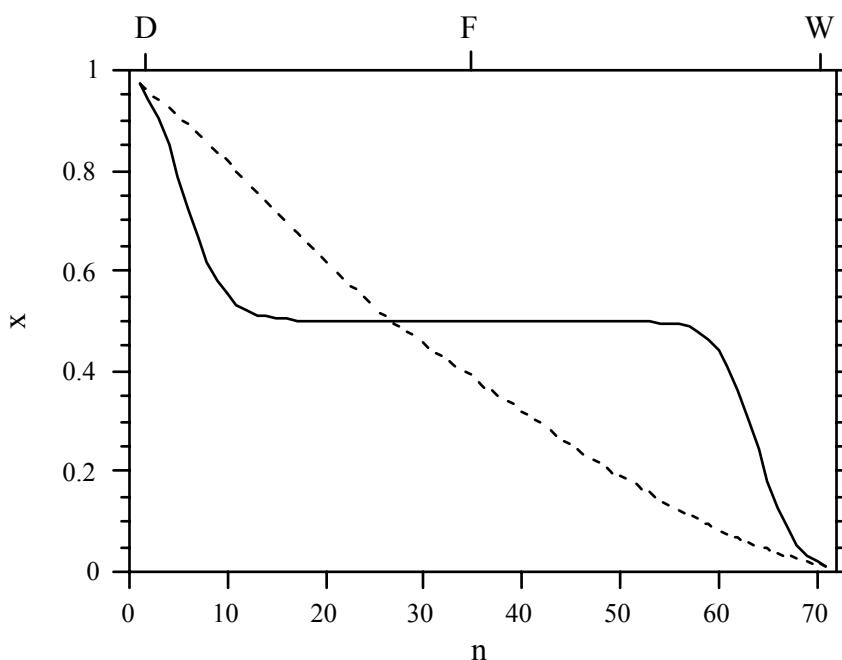


Figure 2. The liquid composition profile x as a function of tray number, counted from the condenser, for conventional (solid) and equal-thermodynamic-distance (dashed) separation of an ideal benzene-toluene system.

5. Optimal temperature profile

The principle of equal thermodynamic distance shows us how to minimize the total dissipation in a trayed column by distributing the dissipation evenly among the trays whatever their number [10, 11]. Above, a general quasistatic step process was optimized, i.e. a process composed of N discrete steps where the system equilibrates fully after each step. The standard description of a distillation column is exactly such a process where it is assumed that gas and liquid come to equilibrium at a particular temperature on each tray. Entropy is produced when the up- and down-moving flows encounter liquid on the next tray at slightly different temperature and composition. The concept of thermodynamic length defined in refs. [1, 6] not only provides a lower bound on dissipation, it also predicts which path will achieve that bound, namely operation with equal thermodynamic distance between the trays.

Two important consequences of this general result are immediate: dissipation (here entropy production) must be equally distributed along the column; and the total dissipation approaches zero as N , the number of trays, goes to infinity (eq. (14)), i.e. the separation becomes reversible. Neither are satisfied in ordinary distillation columns.

In binary distillation 8 extensive quantities are involved on each tray. In the energy picture, these quantities are the entropy, volume, mole number of light

component, and mole number of heavy component for each phase, i.e. for both vapor and liquid: $\mathbf{X} = (S_V, V_V, N_{1V}, N_{2V}, S_L, V_L, N_{1L}, N_{2L})$. This leads to an 8×8 metric matrix

$$\mathbf{M}_U = \begin{array}{cc} & \begin{array}{c} V \quad L \\ \hline \mathbf{M}_U^V \quad \mathbf{0} \\ \hline \mathbf{0} \quad \mathbf{M}_U^L \end{array} \\ \begin{array}{c} V \\ L \end{array} & \end{array} \quad (19)$$

Fortunately a number of relations allows one to reduce the dimensionality of the problem dramatically. First of all, as already indicated by the zeroes, the two physical states are usually considered energetically non-interacting, at once making \mathbf{M}_U block-diagonal. After a partial Legendre transform to the mixed intensive-extensive variables $\mathbf{X} = (T, p, N_1, N_2)$ each of the submatrices \mathbf{M}_U^V and \mathbf{M}_U^L may be further block-diagonalized to

$$\mathbf{M}_U(T, p, N_1, N_2) = \begin{pmatrix} -G_{TT} & G_{Tp} & 0 & 0 \\ G_{pT} & -G_{pp} & 0 & 0 \\ 0 & 0 & G_{N_1N_1} & G_{N_1N_2} \\ 0 & 0 & G_{N_2N_1} & G_{N_2N_2} \end{pmatrix}, \quad (20)$$

where the subscripts indicate partial derivatives. Note that the dependent function is now Gibbs' free energy G corresponding to the variables (T, p, N_1, N_2) .

Constant pressure in the column eliminates the second row and column. Next we recombine the molar quantities N_1 and N_2 into the total amount of material, $N = N_1 + N_2$ and the molar fraction of component 1, $x = N_1/(N_1 + N_2)$ (in the liquid phase, the letter y is traditionally used for the vapor phase). The purpose is once again to effectively eliminate one variable, N since it only describes the total scaling of the process. The metric matrix for the liquid is now down to

$$\mathbf{M}_U^L(T, x, N) = \begin{pmatrix} -G_{TT} & 0 & 0 \\ 0 & -\frac{G_{N_1N_2} N^2}{x(1-x)} & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (21)$$

with an equivalent expression for the vapor. The square of the length element is then

$$\begin{aligned}
(dL_U)^2 &= -G_{TT}^V dT^2 - \frac{G_{N_1 N_2}^V (N^V)^2}{y(1-y)} dy^2 - G_{TT}^L dT^2 - \frac{G_{N_1 N_2}^L (N^L)^2}{x(1-x)} dx^2 \\
&= \left[-G_{TT}^V - \frac{G_{N_1 N_2}^V (N^V)^2}{y(1-y)} \left(\frac{dy}{dT}\right)^2 - G_{TT}^L - \frac{G_{N_1 N_2}^L (N^L)^2}{x(1-x)} \left(\frac{dx}{dT}\right)^2 \right] dT^2
\end{aligned} \tag{22}$$

since the temperatures in the two phases are equal. The vapor and liquid flows N^V and N^L are identified with the actual material flows V and L in the column at that particular tray (see Fig. 1).

The G_{TT} terms are related to the ordinary heat capacities of the vapor and liquid mixtures, respectively,

$$G_{TT}^L = -\frac{L}{T} [x C_1^L + (1-x) C_2^L], \tag{23}$$

where C_i is the molar heat capacity at constant pressure of component i , with a similar equation for the vapor. The terms $G_{N_1 N_2}$ are cross derivatives of the chemical potentials,

$$G_{N_1 N_2}^L = \frac{\partial \mu_2^L}{\partial L_1} = \frac{\partial \mu_1^L}{\partial L_2}, \tag{24}$$

i.e. derivatives of the heavy chemical potential μ_2 with respect to the light flow $L_1 = xL$ and vice versa. The vapor-liquid equilibrium conditions $\mu_1^V = \mu_1^L$ and $\mu_2^V = \mu_2^L$ have also been invoked. For ideal mixtures, $G_{N_1 N_2} = -RT/N$, where R is the gas constant. Again analogous expressions exist for the vapor phase.

Above we have made use of the constancy of pressure to reduce the size of the problem in a fairly straightforward fashion. Mass conservation is applied in a more unusual way. In the traditional description of a distillation tray [2] the material flows of each of the two components entering and leaving a particular tray n are balanced:

$$\begin{aligned}
V^{n+1} y_1^{n+1} + L^{n-1} x_1^{n-1} &= V^n y_1^n + L^n x_1^n \\
V^{n+1} y_2^{n+1} + L^{n-1} x_2^{n-1} &= V^n y_2^n + L^n x_2^n.
\end{aligned} \tag{25}$$

As above, V and L are the vapor and liquid flow rates leaving the tray indicated in the superscript, and x_i and y_i are the molar fractions of component i in the liquid and vapor phases, respectively. These quantities are pictured in Fig. 3.

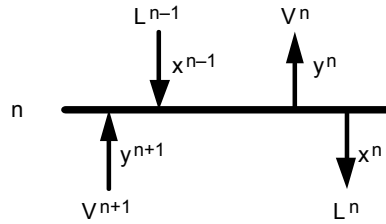


Figure 3. Definition of quantities around tray n.

Calculating the entropy produced in this mixing process of four streams is a bit cumbersome. Instead we consider the entropy produced in connection with the generation of a small bubble of vapor on tray $n+1$ at temperature T^{n+1} and its absorption on tray n. The vaporization creates no entropy since it is an equilibrium process; the vapor of composition (y_1^{n+1}, y_2^{n+1}) is in equilibrium with the liquid of composition (x_1^{n+1}, x_2^{n+1}) from which it is generated at that temperature. On arriving on tray n we split the process of assimilation of the bubble on that tray into two parts: first exchange of only heat and work with the liquid-vapor system on tray n, followed by exchange of materials now at the proper temperature. In the first step the tray fluid acts as the heat and work reservoir for the equilibration, the type of simple horse-carrot process described in Sect. 3. The entropy production in this step is given to first order in the step size by eq. (10) which, when expressed in the mixed intensive-extensive formulation of eq. (3), has only two terms in the sum,

$$\Delta S^{u n} = \frac{1}{2} \left[\Delta \left(\frac{1}{T^n} \right) \Delta U^n - \Delta \left(\frac{p}{T^n} \right) \Delta V^n \right]. \quad (26)$$

This is easier to calculate using the energy picture and the equivalence $\mathbf{M}_U = -\mathbf{T}\mathbf{M}_S$ [9] so that

$$\Delta S^{u n} = \frac{1}{2T^n} [\Delta T^n \Delta S^n - \Delta p \Delta V^n] \quad (27)$$

since the constancy of the pressure knocks out the second term. In this thermo-mechanical equilibration some of the vapor in the bubble (of composition y^{n+1}) will condense so that the bubble volume now contains some liquid of composition x^n plus some vapor of composition y^n due to the new temperature T^n . Introducing the constant pressure saturation heat capacity C_r of the two phase mixture, i.e. the effective heat capacity for gas in equilibrium with liquid [12], so that $\Delta S = C_r \Delta T / T$ makes

$$\Delta S^{u n} = \frac{1}{2} \frac{C_r^n}{(T^n)^2} (\Delta T^n)^2. \quad (28)$$

Once the temperature and the pressure in our bubble have equilibrated to the surroundings, we proceed to the second step during which each fluid phase can mix with the reservoir fluid. Since in a binary mixture T and p fix the composition, this second step occurs reversibly. The total entropy generation for this tray is thus given by eq. (28) above.

On a strictly formal basis we could also recall that the energy and entropy metrics are related through $\mathbf{M}_U = -T\mathbf{M}_S$ [9] and thus quickly arrive at the dissipation between trays n and $n+1$, from eq. (22),

$$\Delta S^{u\ n} = \frac{1}{2} \left(\frac{\Delta L_U^n}{T^n} \right)^2 = \frac{1}{2} \frac{C_r^n}{(T^n)^2} (\Delta T^n)^2, \quad (29)$$

where C_r may be expressed as

$$C_r = V \left[y C_1^V + (1-y) C_2^V \right] - G_{N_1 N_2} V \frac{TV^2}{y(1-y)} \left(\frac{dy}{dT} \right)^2 \\ + L \left[x C_1^L + (1-x) C_2^L \right] - G_{N_1 N_2} L \frac{TL^2}{x(1-x)} \left(\frac{dx}{dT} \right)^2, \quad (30)$$

and where all quantities are related to the particular tray n , and Δ indicates the difference between trays n and $n+1$.

The computational procedure is to integrate eq. (29) from the distillate temperature T_D to the reboiler temperature T_W (both of course given by the required product purities) to obtain the total thermodynamic column length L_S . The distance from one tray to the next must then be fixed at $D_S = L_S/N$ for optimal performance by adjusting the tray temperatures appropriately according to eq. (13).

Obviously such freedom of adjustment does not exist in a conventional adiabatic column where heat is added and removed only in the reboiler and condenser, respectively (Fig. 1). Rather, it is necessary to allow individual heat exchange with each tray to maintain it at the desired temperature (see Fig. 4). This heat addition/removal is of course part of the energy balance used above. The result of the whole calculation is either a graph similar to Fig. 2 specifying the temperature of each tray in the column or a graph of the amount of heat added/removed at each tray.

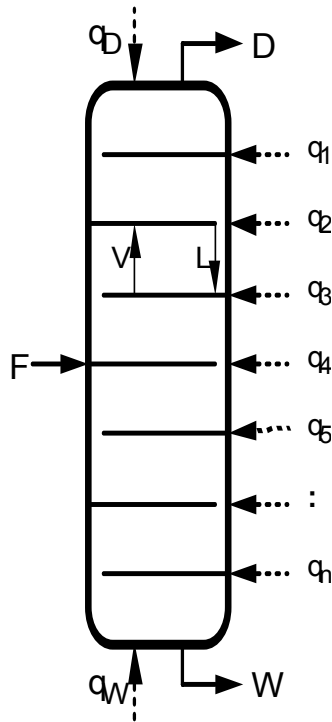


Figure 4. Sketch of an equal-thermodynamic-distance distillation column with feed, distillate, and waste (bottoms) rates F , D , W as in the traditional column Fig. 1, but with heating or cooling on all n trays.

6. Example

Figure 5 is such a graph for a model calculation on an ideal 50/50 benzene-toluene mixture ($x_F=0.5$). Separation of 1 mole of mixture into 99% pure products ($x_D=0.99$ and $x_W=0.01$) requires an exergy expenditure of 191 J in the fully optimized equal thermodynamic distance column with heat exchange on every tray. For comparison the exergy requirement is 842 J, more than a factor of four larger, in a conventional column heated only at the end points as indicated with the two filled circles. If for economic or purely practical reasons one does not wish to mount heat exchangers on every tray in the column, the first step of improvement will be to add just two heat exchangers at appropriate locations, making a total of four positions of heat exchange. Such a column only needs 423 J to do the job, a saving by a factor of two compared to the conventional column.

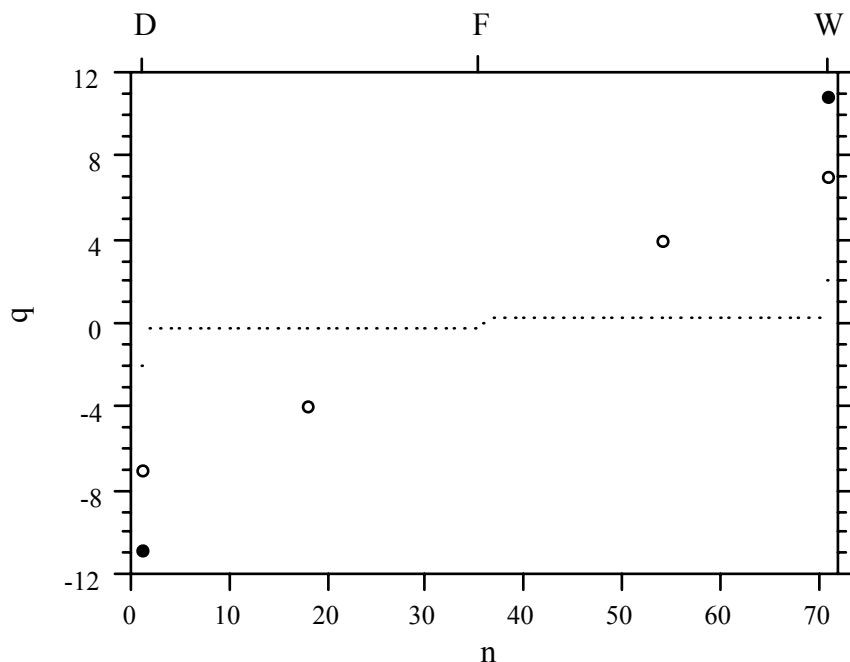


Figure 5. Amount of heat in J added per mole of benzene-toluene feed on the individual trays of a 71-tray column operated in the traditional fashion with heat added only in the reboiler and withdrawn only in the condenser (•); operated according to equal thermodynamic separation specifications with heat added or withdrawn on each tray (◦); and operated with just 2 additional heat exchange points, optimally located (◦).

It should be mentioned that the total amount of *heat* used to perform a certain equal-thermodynamic-distance separation is only marginally different from that required by a conventional column, but a large part of it is used over a much smaller temperature difference than T_W to T_D , leading to a correspondingly smaller *exergy* requirement. The gradual addition and withdrawal of heat lends itself to coupling with other sources and sinks of heat at the plant which might otherwise have been lost or degraded. This distillation system is the first application of the equal thermodynamic distance principle to a chemical system. However, the entire analysis is not restricted to a distillation column but applies equally well to any staged process, be it gas separation by diffusion, staged refrigeration, or batch chemical reactions.

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