



# Quick assessment of binary distillation efficiency using a heat engine perspective



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## ARTICLE INFO

### Article history:

Received 13 April 2016

Received in revised form

13 September 2016

Accepted 16 September 2016

Available online 24 September 2016

### Keywords:

Heat engine

Distillation

Thermodynamic efficiency

Composition dependence

## ABSTRACT

With emphasis on close boiling, (near-)ideal VLE mixtures, this paper links the efficiency of distillation to the binary feed composition and thermal properties of the compounds. The proposed approach, treating the process as a heat engine, allows to directly quantify distillation performance (in terms of energy intensity & efficiency) based on the components boiling points and feed composition. In addition, this approach reviews and formulates simple, approximate and essentially non-iterative calculation procedures to quickly estimate the energy efficiency of distillation. These estimations may be applied to identify opportunities to save significant amounts of energy.

The results show that the reboiler duty for low relative volatility is relatively independent of the heat of vaporization and feed composition, while being reciprocally proportional to the Carnot efficiency of the distillation column. The internal efficiency for distillation of mixtures with low relative volatility has a maximum of about 70% for a symmetrical feed (equimolar ratio) and decreases to zero for unsymmetrical feed compositions approaching infinite dilution. With increasing relative volatility, the maximum efficiency is preserved, but the locus shifts towards lower light component fractions. At very high relative volatility, the internal efficiency increases with decreasing concentration of light component, as typical for evaporators.

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## 1. Introduction

Distillation is historically the most extensively studied, well-known and analyzed separation unit operation. In spite of its benefits and wide-spread use, distillation is by its nature an energy inefficient process and thus it remains a significant contributor to the total use of energy resources worldwide, claiming about 95% of the total energy used in separations and roughly 3% of the total energy used in USA [9].

Proper understanding of distillation processes is clearly needed to elaborate on its efficiency. The energy intensity of processes is coupled with the origin of the energy, and transformation of the used energy to perform the desired separation task, i.e. objective evaluation of the efficiency of such processes. Understanding the energy intensity and efficiency of distillations by simple calculations is of practical importance. One interpretation of efficiency refers to the possible separation efficiency (i.e. product purities)

relative to the number of theoretical (equilibrium) stages. Another interpretation refers to the thermodynamic efficiency (i.e. energy usage) that indicates possible reduction of energy use in separations. Numerous papers deal with the energy intensity and efficiency of distillation based on approaches using second thermodynamic law analysis, such as exergy analysis [8,17,31,32], entropy production analysis [10,16] and related pinch-analysis using equilibrium temperature-enthalpy profiles of distillation columns [5,12]. Table 1 summarizes the most encountered definitions of thermodynamic efficiency for distillation [14].

Ideally, a reasonably accurate estimation of the efficiency can be made on the basis of simple calculations. Some well-known rules of thumb for process feasibility based on properties of the separated compounds have been proposed [7]. These rules of thumb lack quantification of the estimated performance efficiency, and mostly present only boundaries of feasible or infeasible regions of individual process parameters, disregarding any interactions between those. In this work, a quantitative efficiency analysis based on exergy analysis is described.

Exergy analysis based and entropy production based analysis

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**Table 1**  
Definitions of thermodynamic efficiencies for uncoupled and coupled processes.

Efficiency type	Uncoupled process	Coupling efficiency (coupled process)	Overall efficiency (coupled process)
Entropy (S)	–	$\eta_S = \frac{S_{SEP}}{S_H}$	$\eta_S^O = \frac{S_{SEP}}{S_H + S_L}$
Exergy (B)	$\nu_B = \frac{\sum B_{out}}{\sum B_{in}}$	$\eta_B = \frac{B_{SEP}}{B_H}$	$\eta_B^O = \frac{B_{SEP}}{B_H + B_L}$
Energy (E)	$\nu_E = \frac{\sum E_{out}}{\sum E_{in}}$	$\eta_E = \frac{\eta_c \eta_c}{\eta_c^2 + \eta_S \eta_c}$	$\eta_E^O = \frac{\eta_S^O \eta_c^O}{\eta_c^O + \eta_S^O \eta_c^O}$

and optimization methods for distillations were reviewed over a decade ago [11]. The concept of the zero entropy production column was introduced as a theoretical machine with a thermodynamic efficiency equal to unity [13]. The effect of the thermal state of the feed was also studied [2,4]. Various strategies to improve the low thermodynamic efficiency of distillation of binary mixtures were proposed, such as introduction of various heat-pumping technologies [28,29], a diabatic distillation column with side reboilers and condensers [1,3] or advanced internal heat integrated distillation systems [20,24].

This paper analyzes distillation of near-ideal binary systems from a heat engine perspective (considering distillation as a process creating separation work) and investigates the influence of the feed composition and thermal properties of separated compounds on the internal efficiency of the heat engine. Limits of the heat engine analogy arising from additional thermal effects are defined using rigorous exergy analysis of a distillation process. This original approach allows a simple and direct quantification of distillation performance (energy intensity and efficiency) based on boiling points of the separated compounds and the feed composition. Although the efficiency formulas can be also derived from rigorous exergy balance approach [2], and numerical results obtained using pinch-analysis of equilibrium column temperature-enthalpy profiles [4], the approach proposed in this paper is more instructive and natural due to its clear analogy to Carnot's heat engine – especially if the reader is not an expert in exergy analysis and optimization approaches of distillation systems.

The transformation of heat in separation work in a distillation process is decomposed in partial contributions arising from the basic properties and composition of the separated mixture. Such an analysis reveals the challenge associated with distillation of particular binary mixtures and addresses the appropriate modifications of distillation technology, or selection of an alternative separation technique. This paper also provides some practical recommendations to improve the energy efficiency of distillation.

## 2. Results and discussion

Mixing of compounds is a spontaneous irreversible process that occurs with generation of entropy of mixing. Separation of a mixture is basically a reversed mixing process, thus non-spontaneous. As such, it needs delivery of work from outside to be driven [26]. This work can be done by:

- Addition of higher potential heat (e.g. desorption), with possible withdrawal of lower potential heat (e.g. distillation, evaporation)
- Shaft work using pumping or compression (e.g. membrane processes)
- Transport induced by external force-field (e.g. electrodialysis)

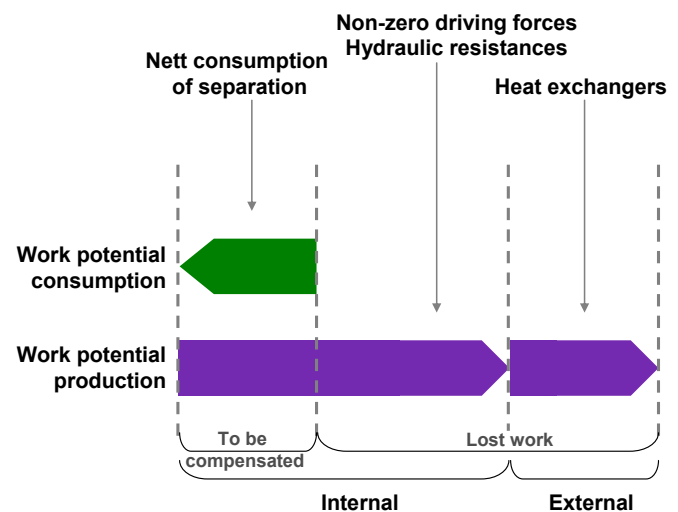
Besides external addition of work, separation operations can utilize the physical potential of the stream to be separated as well (i.e. the mixture to be separated has higher enthalpy, e.g. by elevated pressure, temperature or being saturated vapor instead of

boiling liquid in case of distillation feed). Distinguishing between external work delivery and the physical potential of stream as sources of work is often just a matter of definition of boundaries. For example, physical potential of the stream can be achieved at the expense of external utility (e.g. mechanical energy of reverse osmosis inlet stream due to its pressure acquired by shaft work of a pump, or vaporization of a distillation feed prior to its injection to the column).

Understanding of separation processes as heat engines is advantageous to define the objective efficiency of such processes [2,9,14]. This definition reflects the fact that external work delivered combined with the work potential of the streams can be fully transferred into separation work only if such process works in a reversible mode, which is of course only a theoretical concept. Real irreversible separation processes always use more of the work potential than theoretically needed, and part of it is destroyed, which is reflected in the generation of entropy due to mass and heat-transfer phenomena. Fig. 1 provides a qualitative overview of the utilization of work potential for separation work and entropy production in distillation processes. The process efficiency can be defined as ratio of separation work produced over the work delivered & physical work potential used.

### 2.1. Separation work

The energy intensity of distillation is commonly expressed as heat duty of the reboiler, normalized on the feed or one of the products of importance (e.g. MJ/kg product). Although, such an expression is relevant regarding the expectably proportional consumption of utilities, it does not provide sufficient information on any objective assessment of:



**Fig. 1.** Utilization of delivered work potential in distillation processes for separation and adjacent losses.

- Utilization of such heat by the particular distillation unit
- How the efficiency of the particular distillation can be improved by introduction of either a simple modification of the distillation process, or possibly by applying an alternative type of separation process
- The type of heat utility needed (steam pressure of different levels, different fuels)
- The possibility of integration of the distillation process within larger multiunit process to utilize cheap lower potential heat.
- Minimum energy consumption of refrigeration cooling, when the distillation column operates in a cryogenic mode.

The vast majority of heat added to any distillation column in its reboiler (e.g. by steam) is discharged in its condenser, at a lower temperature level. Furthermore, this heat is possibly not lost, but depending on circumstances potentially available for other operations. An analogous system creating work out of heat is the thermal power-plant where only a minor part of heat obtained from burning fuel is transformed in electrical energy, while the rest of the heat is discharged to cooling utility, thus 'lost' [15]. Following the natural assessment of power-plant efficiency based on the amount of electricity (work) obtained from fuel, a more fundamental approach to the analysis of the efficiency of distillation processes can be based on the definition of this process as an engine transforming heat in separation work. The idea of such analogy, arising from the free energy interpretation of separation processes, has been around for some time [26], but despite its power still not widely applied in analysis of separation processes.

Isothermal separation work can be expressed as the difference of compositional contribution to the Gibbs energy of individual streams. This work is needed to reverse the spontaneous counteraction of mixing. Acceptance of external work has to be depending on excess mixing heat effects coupled with some heat discharge, for isothermal condition to be sustained.

$$\begin{aligned} \dot{W}_{SEP} &= -T_0 \cdot \Delta \dot{S}_{SEP} \\ &= RT_0 \left[ \sum_{\text{out of the system}} \dot{n}_i \sum x_i [\ln(x_i) + \ln(\gamma_i)] \right. \\ &\quad \left. - \sum_{\text{in the system}} \dot{n}_i \sum x_i [\ln(x_i) + \ln(\gamma_i)] \right] \end{aligned} \quad (1)$$

For an ideal mixture (i.e. activity coefficients equal to one) this equation can be simplified to:

$$\begin{aligned} \dot{W}_{SEP,id} &= RT_0 \left[ \sum_{\text{out of the system}} \dot{n}_i \sum x_i \ln(x_i) \right. \\ &\quad \left. - \sum_{\text{in the system}} \dot{n}_i \sum x_i \ln(x_i) \right] \end{aligned} \quad (2)$$

In special cases, when pure components are obtained as products of separation (sharp split) of a binary feed, the previous equation can be further simplified to:

$$\dot{W}_{SEP,id} = -RT_0 \dot{n}_F [x_{FA} \ln(x_{FA}) + (1 - x_{FA}) \ln(1 - x_{FA})] \quad (3)$$

As shown in Fig. 2 (left), the separation work needed to separate an ideal binary feed into pure compounds is a symmetrical function of composition, with a maximum for an equimolar feed and trending asymptotically to zero at the compositional ends (either of compounds being infinitely diluted). When only one of the compounds in the mixture is valuable, it is practical to express the work

needed to remove this compound from the mixture, which is shown in Fig. 2 (right). In Fig. 2 (right), it can be seen that the work consumption (to obtain both compounds pure) related to the separation of 1 mol of particular compound increases relatively mildly at a decreasing concentration of the targeted compound down to a molar fraction of about 0.15. Below this value, the increase of the needed separation work steepens with further decrease of the concentration of the targeted compound. This behavior is a well-known problem in separation technologies, if the desired product is strongly diluted (as typical in biological systems) or if an impurity needs to be removed from the final product to fulfill specifications.

## 2.2. Distillation as heat engine

Separation work delivered to the streams can be obtained from heat in a distillation column as in a Carnot like engine, accepting and discharging heat between the temperature levels of heat supply and heat sink. In the conceptualization of a distillation column as such engine, the internal limitation of heat delivery and withdrawal are the temperatures of vaporization and condensation in reboiler and condenser, respectively. These are represented by the boiling points of the pure compounds at the distillation pressure. The maximum work obtainable from heat accepted in the reboiler can be expressed using the Carnot efficiency:

$$\dot{W}_{\max} = \dot{Q}_{reb} \left( 1 - \frac{T_D}{T_B} \right) \quad (4)$$

Thus, the first quantifiable limitation of distillation performance arises from the difference in boiling points.

The maximum work of Carnot's engine corresponds to the theoretical reversible operation of such equipment with zero internal driving forces. However, in a real distillation column, fully reversible operation (zero driving force) is impossible, and part of the work potential is lost (Fig. 3, left), i.e. entropy is generated, as related in the Gouy - Stodola formula:

$$\dot{W}_{\text{Lost}} = T_0 \Delta \dot{S}_{irr,COL} \quad (5)$$

Lost work is the portion of the total work that is required to overcome the thermodynamic inefficiency due to driving forces within the distillation column [25]. Thus the total work potential of such a Carnot engine can be expressed as:

$$\dot{W}_{\text{Max}} = \dot{W}_{\text{Sep}} + \dot{W}_{\text{Lost}} = T_0 \left( -\Delta \dot{S}_{SEP} + \Delta \dot{S}_{irr,COL} \right) \quad (6)$$

This equation can be used to obtain the internal efficiency of such engine, which leads to the amount of work obtained as compared to the maximum work achievable corresponding to the reversible Carnot engine.

$$\eta_I = \frac{\dot{W}_{\text{Sep}}}{\dot{W}_{\text{Max}}} = \frac{-\Delta \dot{S}_{SEP}}{\Delta \dot{S}_{irr,COL} - \Delta \dot{S}_{SEP}} \quad (7)$$

This definition of internal efficiency is equivalent to the "coupling efficiency" on exergy basis presented in Table 1 [14]. From Eqs. (4)–(7), the separation work follows:

$$\dot{W}_{\text{Sep}} = \eta_I \dot{Q}_{reb} \left( 1 - \frac{T_D}{T_B} \right) = \eta_I \eta_C \dot{Q}_{reb} \quad (8)$$

The definition of efficiency presented by this equation does not include external interactions of the distillation column with its surroundings, and as such this definition of efficiency presents its endo-irreversible limit. In a wider sense, it is more important to know the efficiency of work potential utilization between

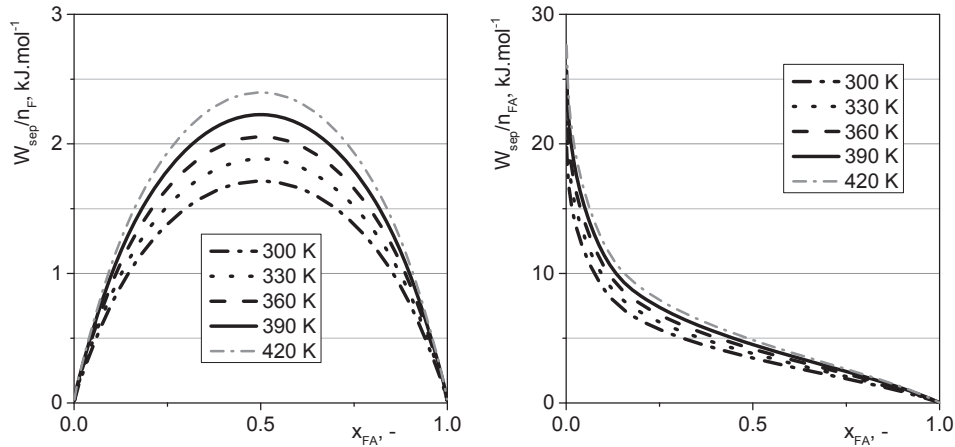


Fig. 2. Separation work required per mole of feed, as a function of the feed composition (left) and per amount of single component in the feed (right), at various temperatures, calculated using Eq. (3).

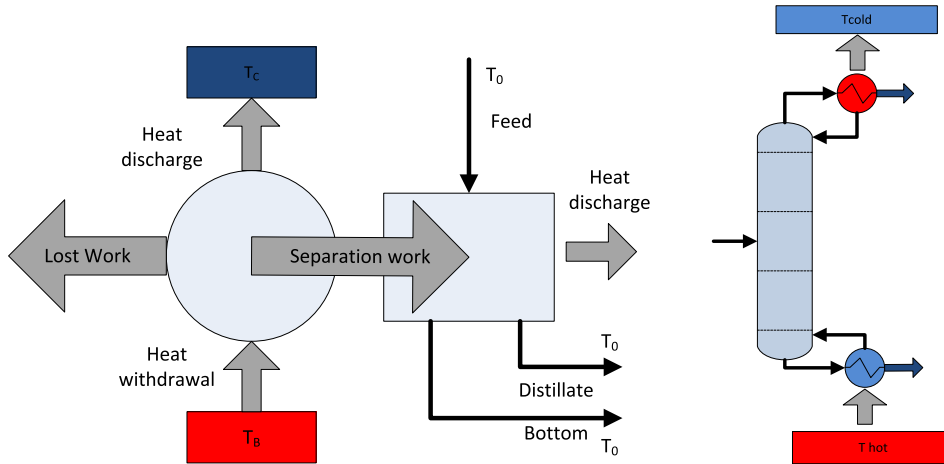


Fig. 3. Distillation column as Carnot heat engine transforming work, within the internal temperature boundaries, into separation work (left) and exo-irreversible limits of heat delivery and discharge (right).

temperatures of external heat supply and heat sink, rather than that of passing heat without external boundaries. When taking the external interactions into account, the efficiency of work potential transformation between external heat source and sink, as shown in Fig. 3 (right) can be defined as follows:

$$\eta_{EXT} = \frac{\dot{W}_{sep}}{\dot{W}_{max-ext}} = \frac{\eta_I \left(1 - \frac{T_D}{T_B}\right) \dot{Q}_{reb}}{\left(1 - \frac{T_{cold}}{T_{hot}}\right) \dot{Q}_{reb}} = \eta_I \eta_{C-ext} \quad (9)$$

From this equation, it follows that the exo-irreversible efficiency pointing to external interactions is proportional to the product of internal efficiency and the endo-reversible Carnot efficiency as presented in Eq. (7). Depending on the situation, the external Carnot efficiency can be independent (heating and cooling by hot and cold utility, respectively) or dependent (heat integration or heat-pumping considerations) on the internal temperature limits presented in Eq. (4). External heat transfer temperatures provide a frame for work potential destruction by the exchange of heat. For example, in scenarios where separated compounds are to be used to fuel the separation process itself, it is common practice to evaluate the net energy intensity of such separation processes by own-

consumption of the product to generate the heat supply needed. Such an analysis can however provide misleading conclusions. Following the known cogeneration principles, the heat can be used to produce work in engines and turbine cycles and possibly only a small part of the temperature potential may be further needed to supply the work needed in the distillation column, reducing the impact of own-consumption. A lot of papers deal with advanced integration strategies of distillation columns to minimize entropy production due to external heat transfer, thus minimizing its effect on net exo-irreversible efficiency, especially using various heat-pumping technologies [18,19]. Further analysis in this paper will regard only endo-reversible limits of the boiling points of the separated compounds in reboiler and condenser, as those are a foundation for any further exo-irreversible considerations.

Describing a distillation using the Carnot engine analogy requires justification for several reasons. Besides the separation work done by distillation, at least one other contribution to work is inevitable, namely the work related to the differences in temperature of feed and products. While equilibration of temperatures of two streams by co-current heat exchange is spontaneous, the reverse process needs work input in the form of heat-pumping. Such a work, reflected in different temperature potential of distillate and bottom, is associated with *thermal de-mixing*. Furthermore,

applying the first law of thermodynamics on the Carnot engine, a positive work term requires the heat flow from the hot reservoir to the engine to be always larger than the heat discharge to the cold reservoir, which is not necessarily case of distillation. Justification and possible limitations of the presented conceptual view on distillation due to these effects can be explained by the flowsheet of a closed cycle of distillation followed by thermal and material mixing operations (Fig. 4).

In the proposed closed cycle, the feed stream is fed as liquid to a distillation column equipped with a total condenser. Distillation is then followed by a co-current heat exchanger of infinite area, where the temperatures of both product streams reach the same value (thermal equilibrium). Consecutively, the heat of both products is further adjusted to the temperature of the feed for reversible heat supply (or heat withdrawal). In this case, reversible means that the hypothetical temperature of heat addition/withdrawal is equivalent to the actual temperature of the streams in that part of the heat exchanger. Afterwards, both streams are isothermally mixed – again with reversible supply/withdrawal of the heat to/from the mixer, respectively. After the mixer, the composition and temperature of the mixture is equivalent to the properties of the feed of the distillation column. All operations are performed at the same pressure. Such a scheme decomposes the work done by the distillation column in two individual contributions to its destruction: first destruction of heat potential of streams by co-current heat exchange, followed by destruction of isothermal separation work by isothermal mixing. Also, the impact and relative importance of additional enthalpy effects is represented by the intermediate temperature adjustment step.

A general work potential (exergy) balance-equation:

$$\sum_{\text{in the system}} \left( \dot{G}_i + \dot{Q}_j \left( 1 - \frac{T_0}{T_j} \right) + \dot{W}_k \right) = \sum_{\text{out of the system}} \left( \dot{G}_i + \dot{Q}_m \left( 1 - \frac{T_0}{T_m} \right) + \dot{W}_n \right) + T_0 \cdot \Delta \dot{S}_{\text{irr}} \quad (10)$$

can be rearranged for the entire cycle as:

$$\sum_{\text{in the system}} \left( \dot{G}_i + \dot{Q}_j \left( 1 - \frac{T_0}{T_j} \right) + \dot{W}_k \right) = \sum_{\text{out of the system}} \left( \dot{G}_i + \dot{Q}_m \left( 1 - \frac{T_0}{T_m} \right) + \dot{W}_n \right) + T_0 \cdot \Delta \dot{S}_{\text{irr}} \quad (11)$$

Taking the boiling point of the distillate as reference (i.e. heat sink, ground) temperature, the previous equation can be rewritten as:

$$\dot{Q}_{\text{reb}} \left( 1 - \frac{T_D}{T_B} \right) + \dot{Q}_{T\text{-adj}} \left( 1 - \frac{T_D}{T_{T\text{-adj}}} \right) + \dot{Q}_{\text{MIX}} \left( 1 - \frac{T_D}{T_F} \right) = T_D \cdot \left( \Delta \dot{S}_{\text{irr},T\text{-MIX}} + \Delta \dot{S}_{\text{irr},\text{MIX}} + \Delta \dot{S}_{\text{irr},\text{COL}} \right) \quad (12)$$

The individual terms on the right hand side represent irreversible production of entropy by:

- Co-current heat exchange (manifesting destruction of thermal de-mixing work done by column)
- Mixing of compounds (manifesting destruction of separation work done by the column, see Eq. (1))
- Irreversible entropy production due to irreversibilities in the column

Using the heat balance of the distillation and the entire cycle, the following equivalences can be obtained:

$$\Delta \dot{H}_{\text{COL}} = \dot{H}_B + \dot{H}_D - \dot{H}_F = \left( \dot{Q}_{\text{reb}} - \dot{Q}_{\text{condenser}} \right) = \dot{Q}_{T\text{-adj}} + \dot{Q}_{\text{MIX}} \quad (13)$$

The temperature of both streams after their co-current heat exchange is between the initial temperatures of those streams. Let us consider a case where the feed is injected at its boiling temperature, which is close to the temperature of the products after their thermal equilibration in the co-current heat exchanger. Such an assumption is, however, only approximately valid, as there is no exact additive mixing rule for boiling points of mixtures based on boiling points and content of pure compounds [21]. Then, the heat needed in the consecutive heat adjusting stage is expectably small

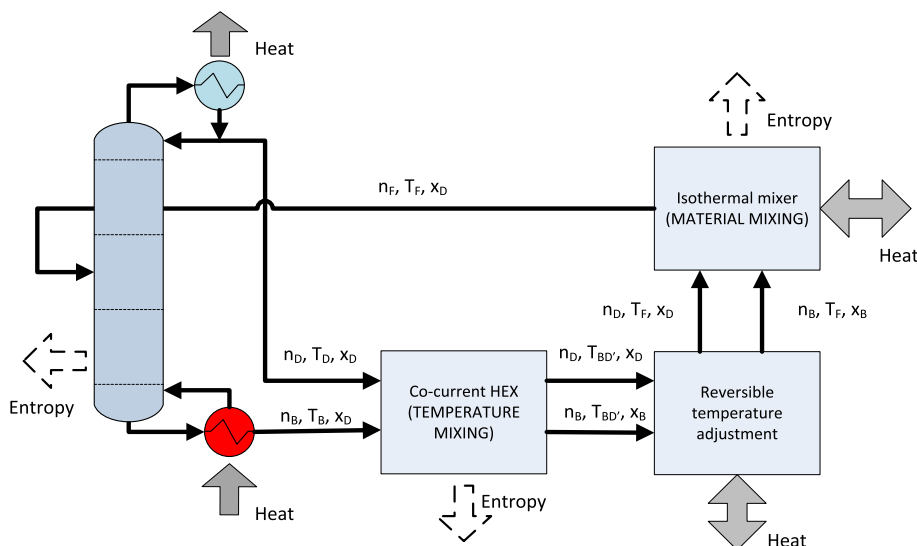


Fig. 4. Cycle of consecutive destruction of distillation work done to the feed, consisting of co-current heat exchange between products in an exchanger of infinite area, followed by reversible temperature adjustment of both products to temperature of the feed, isothermal mixing of products and reinjection of the mixture as feed to the distillation column.



as compared to other terms in that equation and the average temperature of heat addition/withdrawal in this operation can be approximated by the temperature of the feed. Thus, for a saturated liquid feed, Eq. (12) can generally be transformed in Eq. (14).

$$\begin{aligned} \dot{Q}_{reb} \left(1 - \frac{T_D}{T_B}\right) + \Delta \dot{H}_{COL} \left(1 - \frac{T_D}{T_F}\right) \\ = T_D \cdot \left(\Delta \dot{S}_{irr,T-MIX} + \Delta \dot{S}_{irr,MIX} + \Delta \dot{S}_{irr,COL}\right) \end{aligned} \quad (14)$$

This equation was derived with the assumptions of saturated liquid feed and total condenser. It can easily be extended also to partially or fully vaporized feeds, where part of the heat to distillation is delivered by the enthalpic potential of the feed. The corresponding work potential of this heat is lower as compared to the heat obtained in reboiler. The enthalpic potential of the feed corresponds to the 2nd term in Eq. (14). In case when a partial condenser is used, part of heat remains as thermal potential of the distillate. However, discharge of heat by the distillate at this temperature has zero work potential, since it is the heat sink temperature as defined in formulation of Eq. (12). Thus, due to the formal treatment of the vapors of the distillate as condensate of a total condenser, Eq. (14) holds also for a partial condenser when the condensation heat of the distillate is excluded in the second term of Eq. (14). The total change of enthalpy of streams during distillation as compared to the distillation feed can be caused by appreciable excess mixing heat, which is reflected in heat duty of isothermal mixer.

Analyzing the previous equations, a distillation column can be conceptualized as a heat engine transforming the reboiler heat into separation work done at the temperature of the condenser, if:

- The enthalpy difference between products and feed is negligible compared to the heat duty of the reboiler. This suggests a liquid feed close to its boiling point, and negligible excess heat of mixing of the feed mixture.
- The thermal de-mixing work is negligible compared to the separation work done.

If these conditions are satisfied, then Eq. (14) equals Eq. (6) with  $T_0$  being  $T_D$ .

The heat discharged from a Carnot engine is always less than the heat accepted, the difference is the amount of work produced. This is not the case for the cycle of Fig. 4, and on the contrary, equal reboiler and condenser heat duties are expected for this engine when ideal feed mixtures are considered without excess heat of mixing. This obvious paradox can be explained by Fig. 3 (left) illustrating the intrinsic coupling of two processes, i.e. production of work in the Carnot engine and application of this work to separate compounds in the feed. Acceptance of separation work in an isothermal separation process without excess mixing heat effects implies the discharge of its heat equivalent at the temperature of the separation. Hence, closing the energy balance around a distillation column, the net heat effect observed is the discharge of all accepted heat in the condenser, Fig. 3 (left), when negligible excess mixing heat of separated compounds is assumed. Concluding, the Carnot engine parallel for a distillation column is justified, when seen as part of a coupled work generation - application process. Due to the temperature difference in the reboiler and the condenser, there is a difference in work potential of the heat that is accepted in the reboiler, and the heat withdrawn in the condenser, even when quantitatively these heats are equal in size. It is this difference in work potential of the heat flows that is transferred to the separated streams in the distillation process.

Analysis of the thermal de-mixing work starts with considering

the entropy generated in co-current heat exchanger (Fig. 4), which can be expressed as:

$$\Delta \dot{S}_{irr,Q-HEX} = \Delta \dot{S}_D + \Delta \dot{S}_B = \dot{n}_D c_p^D \ln \frac{T_{BD}}{T_D} + \dot{n}_B c_p^B \ln \frac{T_B}{T_{BD}} \quad (15)$$

At the same time, from the heat balance of this heat exchanger it follows:

$$\dot{n}_D c_p^D (T_{BD} - T_D) = \dot{n}_B c_p^B (T_B - T_{BD}) \quad (16)$$

For the case of similar heat capacities of both products  $c_p^D = c_p^B = c_p$ , the next formula holds:

$$\begin{aligned} \Delta \dot{S}_{irr,Q-HEX} = \dot{n}_F c_p [\ln(x_{FA} T_D + (1 - x_{FA}) T_B) - x_{FA} \ln(T_D) \\ - (1 - x_{FA}) \ln(T_B)] \end{aligned} \quad (17)$$

Comparing Eq. (12) with ideal separation work in Eq. (3), the following ratio can be obtained for the thermal de-mixing work and the ideal separation work:

$$\begin{aligned} \frac{\dot{W}_{T-demix}}{\dot{W}_{SEP,id}} &= \frac{-T_0 \Delta \dot{S}_{T-mix}}{-T_0 \Delta \dot{S}_{SEP,id}} \\ &= \frac{c_p [\ln(x_{FA} T_D + (1 - x_{FA}) T_B) - x_{FA} \ln(T_D) - (1 - x_{FA}) \ln(T_B)]}{R [x_{FA} \ln(x_{FA}) + (1 - x_{FA}) \ln(1 - x_{FA})]} \\ &= \frac{c_p Z}{R} \end{aligned} \quad (18)$$

The parameter Z was calculated for various differences of boiling points of pure compounds obtained in distillate and bottom  $T_B$  and  $T_D$  and feed compositions. In Fig. 5, the parameter Z is shown over the entire compositional range. For  $\Delta T_b$  of 30 K or 100 K, the value does not exceed  $1.6 \cdot 10^{-3}$  and  $1.5 \cdot 10^{-2}$ , respectively. Table 2 provides examples of calculations for various representative chemicals.

Based on this analysis, the thermal de-mixing work can be generally neglected for close-boilers that differ less than 30 K in boiling point, and when their molar isobaric heat capacities are relatively small (e.g.  $380 \text{ J mol}^{-1} \text{ K}^{-1}$  for dodecane). Otherwise, the thermal de-mixing work should be regarded as physical upgrading

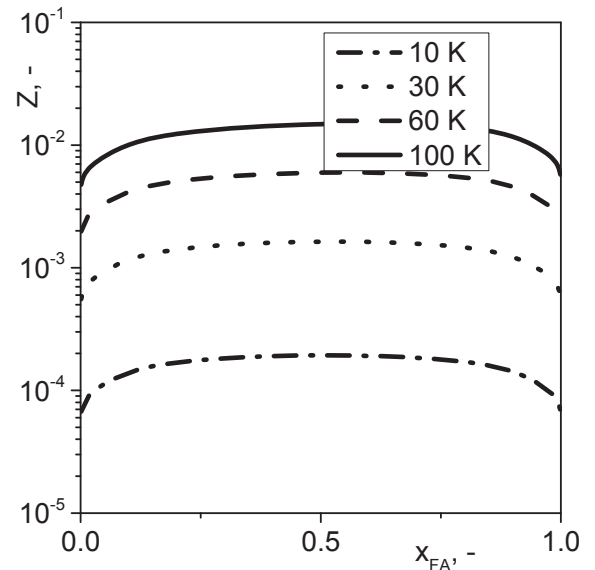


Fig. 5. Dependence of parameter Z from Eq. (18) on the feed composition, for various differences between boiling points of the distilled compounds (at  $T_D = 300 \text{ K}$ ).

of streams and has to be included in analysis. In case the thermal separation work is not negligible, it needs to be included along with separation work in the definition of efficiency in Eq. (7).

### 2.3. Internal efficiency of distillation

Although in Eq. (7) a definition was given for the internal efficiency of distillation processes, no relation was provided to express this internal efficiency to properties of the feed, i.e. composition and relative volatility. In the following analysis, for ideal VLE binary mixtures, that derives this relation, the following assumptions are considered:

- The distillation feed is introduced as a saturated liquid (at boiling point)
- The heat of evaporation of both compounds is sufficiently similar to be approximated by a single value, and apparent enthalpy changes along the column due to the temperature profile can be neglected as compared to the heat exchanged due to evaporation/condensation. The specific enthalpy of boiling liquid and saturated vapor can be considered parallel along the entire compositional range [27]. The operating lines are described in both stripping and rectifying sections by linear functions of the composition in molar ratio expression. This is reflected in the constant molar overflow assumption. Introducing this assumption, all temperature induced effects on enthalpy are also a-priori negligible.
- The relative volatility of the two compounds in the mixture can be considered constant in the range of compositions and temperatures. This implies the validity of Raoult's law, thus activity coefficients can be considered to be equal to 1. For such mixtures, equal values of evaporation enthalpies induce minimum change of relative volatility due to temperature changes along the column. Validity of Raoult's law also implies that separation work can be calculated using Eq. (2) or Eq. (3) for a sharp split.
- Analysis is done for minimum reflux ratio conditions. As the real reflux ratio is usually 1.1 to 1.2 times larger value than the minimum reflux ratio, the conclusions can be extended to efficiency of real distillation processes.
- Pressure drop induced effects are neglected in this basic analysis.

In formulation of a relation describing the efficiency of adiabatic distillation columns, actual reboiler and condenser heat duties need to be correlated to properties of the feed using design calculations. Such link can be provided following the well-known McCabe Thiele's method [22], which is excellent for explaining aspects of binary distillation processes. The operating lines in both column sections are graphical representations of the material balances of the parts between its ends (distillate or bottom stream) and inlet and outlet from the boundary tray of such mass balance envelope.

The material balance coupling the composition of streams can under assumption of constant molar overflow be coupled to a constant reflux ratio. This idea is essential for the graphical construction of McCabe-Thiele diagrams, since it provides operation

lines to be straight.

$$\dot{n}_L = \frac{x_{DA} - y_A}{y_A - x_A} \dot{n}_D = R \dot{n}_D \quad (\text{rectifying section}) \quad (19)$$

$$\dot{n}_V = \frac{x_A - x_{BA}}{y_A - x_A} \dot{n}_B = B \dot{n}_B \quad (\text{stripping section}) \quad (20)$$

For saturated feed, the relation between the flows of vapor and liquid in both sections can be obtained from the total phase flow balance in the stripping section:

$$\dot{n}_V = \dot{n}_L + \dot{n}_D \quad (21)$$

The equilibrium composition of binary mixtures can be expressed as follows:

$$y_A = \frac{\alpha x_A}{1 + (\alpha - 1)x_A} \quad (22)$$

Combining the above equations, the compositional dependence of the minimum flows in both phases follows:

$$\dot{n}_{L\min} = \frac{\alpha x_A - x_{DA}[1 + (\alpha - 1)x_A]}{\alpha x_A - x_A[1 + (\alpha - 1)x_A]} \dot{n}_D = R_{\min} \dot{n}_D \quad (23)$$

$$\dot{n}_{V\min} = \frac{(x_A - x_{BA})[1 + (\alpha - 1)x_A]}{\alpha x_A - x_A[1 + (\alpha - 1)x_A]} \dot{n}_W = B_{\min} \dot{n}_B \quad (24)$$

The minimum amount of liquid flow corresponding to the minimum reflux ratio increases with decreasing content of the lighter compound.

The operating lines in case of ideal VLE cross each other and the equilibrium line at the feed stage that corresponds to the feed pinch-point. Minimum liquid and vapor flows at such conditions represent net minimum flows of the liquid and vapor in both sections and relates them, closing the heat balance of the column. As the minimum reflux ratio can be related to composition of the feed, the design calculation of minimum liquid and vapor flows are long known and can be found in more detail in Ref. [30].

For a boiling liquid feed, in the case of the limiting scenario of a total split (100% yield of products,  $x_{DA} = 1$ ,  $x_{BA} = 0$ ), the minimum refluxed liquid flow above the equilibrium stage and the balance over the column as:

$$\dot{n}_{L\min} = \frac{\dot{n}_F}{\alpha - 1} \quad (25)$$

This equation is valid without either assumption of constant molar overflow, or ideal VLE behavior, and it is generally valid for actual conditions around the feed stage, with the limitation of the absence of tangent pinch points [6]. Using the assumption of constant molar overflow, and the mass balance for a sharp split, the previous equation can be expressed in terms of minimum reflux ratio and distillate flowrate:

$$R_{\min} = \frac{1}{x_{FA}(\alpha - 1)} \quad (26)$$

As a result of the assumption of the equal evaporation heats of

**Table 2**  
Maximum de-mixing work vs separation work for various components, at 30 K and 100 K difference of boiling points.

Component	$\frac{c_p}{R}$	$\frac{W_{F-demix}}{W_{SEP,id}}$ at $\Delta T_b = 30 \text{ K } x_{FA} = 0.5$	$\frac{W_{F-demix}}{W_{SEP,id}}$ at $\Delta T_b = 100 \text{ K } x_{FA} = 0.5$
Water	9	1.5%	14%
Ethanol	13.5	2.2%	20%
Dodecane	45.2	7.3%	68%

both separated compounds, and the minimum enthalpy difference between a boiling liquid feed and the products, the following formula for reboiler/condenser duty required can be obtained.

$$\begin{aligned}\dot{Q}_{reb} &= \dot{Q}_{cond} = \dot{n}_D(R_{min} + 1) \cdot \Delta_v H = x_{FA} \dot{n}_F (R_{min} + 1) \Delta_v H \\ &= x_{FA} \dot{n}_F \left( \frac{1}{x_{FA}(\alpha - 1)} + 1 \right) \Delta_v H\end{aligned}\quad (27)$$

This equation has two asymptotic ends, depending on the value of relative volatilities. One asymptotic end is the distillation of a mixture with low relative volatility (close boiling mixtures). In that case, the heat calculated is not dependent on the composition of the feed, but rather proportional to the molar amount of the feed in total.

$$Q_b = \frac{\dot{n}_F \Delta_v H}{(\alpha - 1)} \quad (28)$$

At large values of relative volatility, the other limiting scenario corresponds to practically single stage evaporation with zero reflux.

$$Q_b = x_{FA} \dot{n}_F \Delta_v H \quad (29)$$

In this case, the equilibrium concentration is proportional to the heat of phase change of the light component only. Increasing the relative volatility, the difference in evaporation heats of both compounds generally increases. Thus, the initial assumption of the constant molar overflow diminishes. Also, different evaporation heats induce a temperature dependence of relative volatility, thus it cannot be generally considered constant along a distillation column, even when the validity of Raoult's law is preserved. Despite this fact, Eq. (27) provides valuable insights in distillation performance change for different relative volatility of compounds.

Fig. 6 (left) plots the ratio of reboiler duty to the heat needed to evaporate the feed, while Fig. 6 (right) plots the reboiler duty normalized to the heat needed to evaporate the light component, along the concentration range of the light component at various values of relative volatility. Even for common relative volatilities of 1.5 or 2, the heat consumption is relatively independent on the concentration of the separated species, corresponding to the asymptotic scenario presented in Eq. (28). Moreover, even for much larger values of relative volatility ( $\alpha = 5-10$ ), the heat consumption is considerably larger than the heat needed to evaporate the light component. This behavior is more severe for cases, where the light

compound is diluted in the feed. Overall, this shows the limits of applicability of the popular belief that the heat consumption in the reboiler can be approximated by the heat needed to evaporate the light component, except for the case of very large values of relative volatility (evaporation process) in combination with large concentrations of evaporated species in the distillation feed.

Eqs. (27)–(29) reflect an intuitive understanding of a distillation process: that the heat duty of a distillation column scales up proportionally to the amount of feed, and with the evaporation heat of compounds to be separated. However, as a paradox, the maximum separation work that is possibly delivered to the products by the column, Eqs. (1)–(8), scales only with the molar amount of feed and the difference in boiling points being seemingly independent from the evaporation heat of both compounds. This apparent paradox can be explained by the next equations that express internal efficiency of a distillation column as defined in Eq. (7). Combining Eqs. (3) and (27), the following formula for the product of the Carnot efficiency and the internal efficiency can be obtained.

$$\eta_I \eta_C = \frac{\dot{W}_{SEP,id}}{\dot{Q}_{reb}} = \frac{-RT_D \dot{n}_F [x_{FA} \ln(x_{FA}) + (1 - x_{FA}) \ln(1 - x_{FA})]}{x_{FA} \dot{n}_F \cdot \Delta_v H \left( \frac{1}{x_{FA}(\alpha - 1)} + 1 \right)} \quad (30)$$

From this equation, an expression for the internal efficiency can be obtained.

$$\eta_I = \frac{-RT_D [x_{FA} \ln(x_{FA}) + (1 - x_{FA}) \ln(1 - x_{FA})]}{\Delta_v H \left( \frac{1}{(\alpha - 1)} + x_{FA} \right) \eta_C} \quad (31)$$

Using the Clausius-Clapeyron equation, the natural logarithm of the relative volatility of two compounds of about the same evaporation heat can be obtained, using their boiling points at the pressure of distillation.

$$\ln(\alpha) = -\frac{\Delta_v H}{R} \left( \frac{1}{T_B} - \frac{1}{T_D} \right) = \frac{\Delta_v H}{RT_D} \eta_C \quad (32)$$

The logarithm of the relative volatility scales up with the evaporation heat of the compounds, thus for the relative volatility to remain constant, the difference in boiling points should increase with decreasing evaporation heat, and vice versa. Changing the pressure, the Carnot efficiency in Eq. (32) tends to remain constant

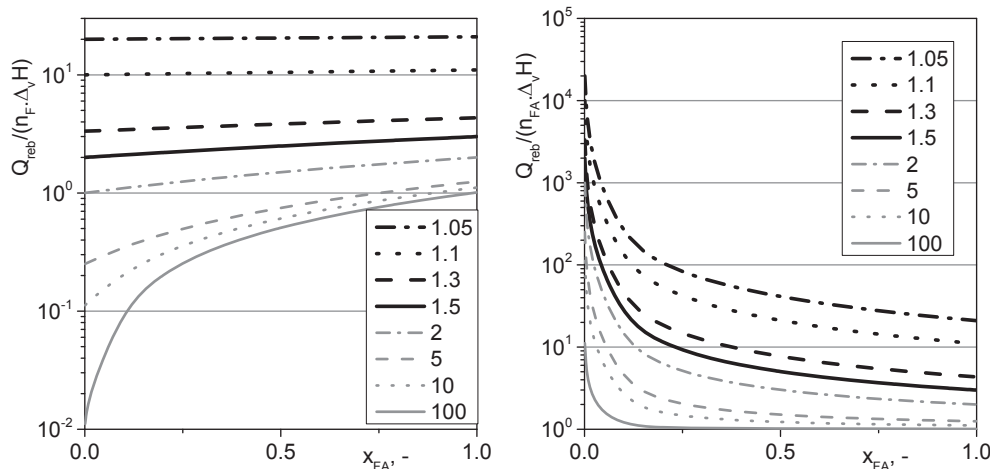


Fig. 6. Feed composition dependence of the ratio of reboiler duty of distillation column sharply separating the feed in pure compounds per amount of heat needed to evaporate the whole feed (left) and the heat needed to evaporate the light component in the feed (right).



[23], thus the relative volatility is reciprocally proportional to the temperature of the distillation.

Following Eq. (32), both a small difference in boiling points, and a low heat of evaporation results in low relative volatility. This effect explains the paradox described earlier. The natural logarithm of the relative volatility divided by the universal gas constant and the boiling point of the more volatile compound, can be seen as the maximum work obtainable by evaporation of 1 mol of the feed mixture - in analogy with Eq. (8). Using Eq. (31) and (32), the formula for internal efficiency of the column can be rewritten as a function of composition and relative volatility.

$$\eta_I = \frac{x_{FA} \ln(x_{FA}) + (1 - x_{FA}) \ln(1 - x_{FA})}{\ln(\alpha) \cdot \left( \frac{1}{(\alpha-1)} + x_{FA} \right)} \quad (33)$$

Eq. (33) can be also derived by using rigorous exergy analysis, and its validity was verified on several real distillation systems [2]. Fig. 7 (left) illustrates the concentration dependence of the internal efficiency using Eq. (33) at various values of relative volatility. This is in agreement with observations based on other approaches reported in literature [2,4]. For relatively low values of relative volatility (up to 2), the efficiency is symmetrical with a maximum of about 70% corresponding to the symmetrical (equimolar) mixture. The maximum efficiency of 70% for low relative volatility mixtures, and efficiency values of 32% (for feeds containing 10% and 90% of light component) are significantly above the generally perceived distillation efficiency of 10% and below. One of the effects causing decreased real internal efficiency is pressure drop [4]. However, many distillation papers present exo-irreversible efficiency defined in Eq. (9) as thermodynamic efficiency of distillation systems. Based on this discrepancy, it can be seen, that the majority of work potential is generally lost due to heat transfer driving force (in condenser and reboiler) and not in the distillation column itself [2]. The natural logarithm of the relative volatility for its values close to one can be approximated as:

$$\ln(\alpha) = \alpha - 1 \quad (34)$$

Thus, for low values of relative volatility, Eq. (33) can be rewritten (by neglecting close to zero terms) as follows – similar to ideal sharp split separation work represented by Eq. (3):

$$\eta_I = -(x_{FA} \ln(x_{FA}) + (1 - x_{FA}) \ln(1 - x_{FA})) \quad (35)$$

For low relative volatilities then, the heat consumption in the reboiler can be calculated as:

$$\dot{Q}_{reb} = \dot{n}_F \frac{RT_D}{\eta_C} \quad (36)$$

The heat duty for lower relative volatilities can independent of feed composition be approximated by this formula, with the heat proportional to the amount of processed feed and reciprocally proportional to the Carnot efficiency arising from the boiling points of both compounds. This in agreement with the results presented in Fig. 6 (left). This formula also shows that no influence of the evaporation heat on the heat duty in distillation processes can be expected for distillation of mixtures with low relative volatility. Decreasing the distillation pressure, the temperature in the numerator of Eq. (36) increases linearly proportionally, while the Carnot efficiency tends to remain constant as mentioned for relative volatility, Eq. (32). In scenarios when heat duty is of primary concern due to unfavorable work potential destruction resulting from external heat transfer, decreasing the distillation pressure is a possible strategy to decrease the severity of this issue, e.g. cryogenic distillations of small close boiling hydrocarbons C<sub>2</sub> and C<sub>3</sub>[2].

The symmetrical decrease of the internal efficiency to zero, for the feed approaching any compositional end, points to large waste of work potential in distillation of strongly diluted mixtures. This is proportionally translated to exo-irreversible efficiency, Eq. (9). Introduction of side reboilers or condenser is not likely a viable option too, due to the large destruction of saved work potential for the same heat consumed by external heat transfer driving forces. Thus, as alternative, using mass separation agents is a better prospect for separation of such mixtures.

Increasing the relative volatility, the maximum in the internal efficiency is almost preserved, while the locus of the maximum moves towards lower concentrations of the light compound, as shown in Fig. 7 (left). However, the limiting internal zero efficiency for infinite dilution of both compounds is still preserved. The evaporation heat is translated into separation work obtainable from heat, Eq. (8), due to its influence on the relative volatility and thus internal efficiency, Eqs. (32) and (33). For cases when the feed is not a saturated liquid but fully vaporized, the maximum in Fig. 7 is preserved and shifts symmetrically with the composition of heavy compound. At the same time, the maximum efficiency can be preserved in the compositional range by suiting the ratio of liquid and vapor between the limiting cases of boiling liquid and

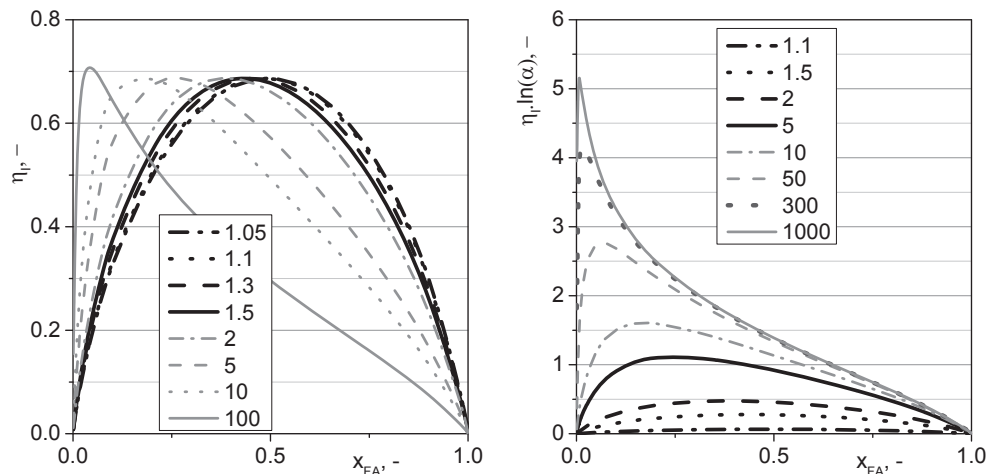


Fig. 7. Internal efficiency of distillation process (left), and work obtained by adding heat equivalent of evaporation of 1 mol of volatile compound (right) as function of feed composition with relative volatility of the mixture as varied parameter.

saturated vapor feeds [2,4]. However, such a result is of limited practical importance. When taking exo-irreversible implications into account, if the feed needs to be vaporized by the same heat source as used in reboiler, then all potential improvement of internal efficiency by a suitable thermal state of feed are to be destroyed by external heat transfer.

The asymptotic endpoint of the moving maximum in Fig. 7 (for very large values of relative volatility) is reflected in the increasing efficiency of evaporators with decreasing concentration of the light component, as opposed to distillation of low relative volatility mixtures. Fig. 7 (right) shows the concentration dependence of the separation work done by the equivalent of heat needed to evaporate the feed. Increasing the relative volatility, all lines asymptotically approach the master line (with deviations in the lower concentration regions) of the same shape as in Fig. 2 (right). Intermediate behavior can be observed for low content of more volatile component, where a larger value of relative volatility is needed for achievement of limiting evaporation-like behavior.

For evaporation processes, the Carnot efficiency is defined by external temperature limits of the process, since the heavy product is non-volatile for all practical reasons. At large relative volatilities, the product of the internal efficiency and the Carnot efficiency in Eq. (30) can be shown using Eqs. (3) and (29) to be reciprocally proportional to the evaporation heat.

$$\eta_i \eta_C = \frac{\dot{W}_{SEP,id}}{\dot{Q}_{reb}} = \frac{-RT_D [x_{FA} \ln(x_{FA}) + (1 - x_{FA}) \ln(1 - x_{FA})]}{x_{FA} \cdot \Delta_v H} \quad (37)$$

Thus, as opposed to distillation of close boiling point mixtures, the evaporation heat of the more volatile species is the governing parameter in estimation of the internal efficiency of evaporation processes.

#### 2.4. Example cases

To investigate the applicability of the short-cut efficiency calculation on real binary distillations, three industrial distillation cases were studied. The three cases were simulated using the DSTWU module in Aspen Plus with the Peng-Robinson equation of state as benchmark. The internal efficiency was calculated based on these process simulations, and were compared with the short-cut method. The first two cases were C<sub>3</sub> splitter columns fractionating propane-propylene mixtures at 3 bar and 15 bar. The respective average relative volatility was 1.22 and 1.14, respectively. The third case was a distillation of butane and pentane (C<sub>4</sub>–C<sub>5</sub>) at 3 bar with an average relative volatility of 2.83. For each case, three feed compositions were evaluated, i.e.  $x = 0.05$ ,  $x = 0.50$  and  $x = 0.95$ . The heat duties were estimated at a reflux ratio of 1.2 times the minimum reflux ratio, and for boiling liquid feeds. To mimic close to sharp separations, a conservative estimate of 99% recovery of each compound in its natural product cut was supposed. Pressure drop effects were neglected.

For each process, the maximum work input was calculated based on heat duty of the reboiler, the Carnot efficiency was calculated with Eq. (4) using the temperatures in the condenser and reboiler. The actual achieved work was estimated from the

difference in the Gibbs energy flows of feed and product streams. The internal efficiency was calculated from the actual achieved work and the maximum work output using Eq. (7). These efficiencies, tabulated in Table 3, were compared to the internal efficiency calculated with Eq. (31) (values in between brackets). It follows from the comparison that despite additional thermal effects on the Gibbs energy, non-perfect sharp split, and reflux ratios considerably larger than their minimum value, Eq. (31) provides reasonable estimates on actual distillation column performances, and is validated for its fast screening. The largest deviations were observed for feeds containing 50 mol % of both compounds, where the effect of the larger reflux ratio seems to play an important role. In all three cases deviations ranging from 11% to 19% of the estimated internal efficiency were observed for the equimolar feed, while the deviations were only a few percent at the dilute feeds.

Also, comparing the calculated heat duties of 64 and 79 MW for distillation of 100 t h<sup>-1</sup> of 50:50 C<sub>3</sub> mixture at pressures of 3 and 15 bars, respectively correlate well with the simple expression in Eq. (36) and the respective condenser temperatures presented in Table 3.

The low Carnot efficiency in case of C<sub>3</sub> splitting results in large reboiler duties, while the actual internal efficiency is not poor for close to 50:50 feeds. In such cases, a significant reduction in utility heat duty may be realized by application of heat-pump technologies. For strongly diluted feeds (e.g.  $x_{FA} = 0.05$ ), the internal efficiency is low, and heat pump technology is less favorable, in these cases affinity operations such as liquid-liquid extraction or adsorption are suggested to remove minor impurities.

### 3. Practical recommendations

Understanding of the origin of the efficiency of simple distillation processes enables to address the issue appropriately by alternative technology. The key to minimizing the lost work is to design a process that is as close as possible to being reversible, while still economical [25]. Following the analysis of the energy efficiency of distillation, it can be concluded that the lost work (thermodynamic irreversibilities) include: heat transfer or/and mixing between fluids of different temperatures; mass transfer between streams that are not in equilibrium. The heat transfer related lost work is reflected for example in the temperature differences between the inlet vapor and inlet liquid on each stage. The lost work due to heat transfer represents a large part of the total lost work. Sometimes, inter-reboilers can be employed (using waste heat or heat integration) to increase internal efficiency and thus reduce the high pressure steam requirements in distillations of wider-boiling compounds. Similarly, inter-condensers are recommended for sub-ambient operation in order to reduce the expensive refrigeration requirements.

Summing up, based on this work the following practical recommendations can be made to increase the overall efficiency of distillation processes.

- Pre-concentrate the feed by other separation methods (e.g. liquid-liquid extraction, adsorption, membrane separation, etc),

**Table 3**

Comparison of simulation results with internal efficiency calculation using Eq. (31) (the values in between brackets) for three studied cases. Simulated internal efficiencies are based on the Gibbs energies of the streams.

Case	$T_B$ , K	$T_D$ , K	$\eta_C$	$\eta_i$ $x_{FA} = 0.05$	$\eta_i$ $x_{FA} = 0.50$	$\eta_i$ $x_{FA} = 0.95$
Propane-propene (3 bar)	258.8	252.5	2.4%	21% (21%)	62% (69%)	19% (18%)
Propane-propene (15 bar)	316.8	309.0	2.4%	17% (21%)	58% (69%)	17% (19%)
Butane-pentane (3 bar)	345.1	305.4	11.5%	28% (31%)	55% (63%)	14% (13%)

especially in case of highly diluted streams, e.g. when the internal efficiency drops below 20%.

- Employ heat pumps (e.g. vapor recompression, compression-resorption) to recover and re-use the low temperature heat discharged to avoid large utility heat duty. This is typically the case for close-boiling components, where the difference between the reboiler and condenser temperatures is small (as a rule of thumb below 15 °C), hence, the Carnot efficiency of distillation as heat engine is low.
- Reduce the operating pressure to decrease further the heat duty required by distillation by increasing the relative volatility. Adjust relative volatility, so that maximum internal efficiency corresponds to feed composition [2].

For the sake of completeness and reader's convenience, a few more generic suggestions are also included [14]:

- Improve energy utilization by appropriate retrofit of internals (i.e. optimize the heat duty changes associated to the change in the number of stages).
- Thermally integrate distillation columns (e.g. fully thermally coupled distillation), wherever possible, to re-use heat of various (intermediate) temperature levels.
- Apply energy integration concepts (e.g. multi-effect distillation).
- Use non-adiabatic (or close to diabatic) distillation systems (e.g. HiDiC technology)
- Explore the possibility of using of inter-reboilers (when waste heat is available or the heating utility is expensive) and/or inter-condensers (when refrigeration is expensive).
- Pre-heat the feed streams (e.g. by feed-effluent heat integration, or using waste heat).
- Feed directly to downstream units (i.e. without intermediate cooling/condensing).

#### 4. Conclusions

Treating separation processes as heat engines that create separation work allows the analysis of their performance in a consistent and straightforward way, and relates the internal efficiency to the composition of the mixture and the thermodynamic properties of the components to be separated. Employing this approach, the internal efficiency of distillation is based on the separation work realized from the work potential used. Basically, a distillation column can be treated as a heat engine that transforms heat between the endo-reversible temperature limits defined by the boiling points of the components separated (i.e. reboiler and condenser temperatures).

Employing this approach, the internal efficiency is proportionally translated to the efficiency of external work potential utilization, for any thermal interaction with other parts of the process. The internal efficiency of distillation can be expressed as a function of the relative volatility of the components and of the feed composition. The overall efficiency is the product of the Carnot efficiency and the internal efficiency.

In case of distilling mixtures with low relative volatility, the reboiler duty is independent of the feed composition and the heat of vaporization of the separated compounds, while being reciprocally proportional to the Carnot efficiency of such a column. The internal efficiency in this case has a maximum of about 70% for symmetrical equimolar feed composition, and decreases to zero for feed compositions approaching infinite dilution of either component.

For larger values of relative volatility, the maximum internal efficiency is preserved but the locus of the maximum shifts towards lower concentrations of light component. The limiting end is the increase of internal efficiency with decreasing concentration of

light component (typical for evaporators). Understanding of efficiency of distillation processes enables a guided approach in the synthesis of more efficient separation processes.

#### Acknowledgements

This is an ISPT (Institute for Sustainable Process Technology) project.

#### Nomenclature

##### Symbols

$\alpha$	relative volatility
$\gamma$	activity coefficient, - $\eta$ efficiency, - $c$ specific molar heat capacity, J mol K <sup>-1</sup>
$G$	flux of Gibbs energy, J s <sup>-1</sup>
$H$	flux of material stream enthalpy, J s <sup>-1</sup>
$n$	molar flux, mol s <sup>-1</sup>
$R$	universal gas constant, 8.314 J kmol <sup>-1</sup> K <sup>-1</sup>
$R$	reflux ratio
$Q$	heat flux, J s <sup>-1</sup>
$S$	entropy flux, J s <sup>-1</sup> K <sup>-1</sup>
$T$	thermodynamic temperature, K
$W$	work flux, J s <sup>-1</sup>
$x$	molar fraction
$Z$	parameter defined in Eq. (18)

##### Indices

$O$	corresponding to reference state
$A$	more volatile (light) component of binary mixture
$B$	corresponding to bottom of column
$BA$	corresponding to more volatile (light) component in bottom product stream
$BD$	corresponding to streams after temperature equilibration of column's distillate and bottom products
$C$	Carnot
$COL$	in column
$COLD$	corresponding to utility accepting heat in condenser
$D$	corresponding to distillate
$DA$	corresponding to more volatile (light) component in distillate stream
$EXT$	taking external heat transfer into account
$F$	feed
$FA$	corresponding to more volatile (light) component in feed stream
$Hot$	corresponding to utility delivering heat in reboiler
$i$	regarding $i$ -th compound entering system
$j$	designation of heat stream in the system
$I$	internal, corresponding to endo-reversible limits(excluding external heat transfer)
$id$	at ideal mixing conditions
$in$	referring to streams into the process (activity coefficients equal to 1, Raoult's law is valid)
$irr$	irreversible (produced due to irreversibility)
$l$	regarding $l$ -th compound entering system
$L$	liquid
$lost$	corresponds to flux of property or potential destruction due to irreversibility
$m$	designation of heat stream out of the system
$max$	maximum, corresponding to theoretical reversible operation reversible
$min$	corresponding to pinched column conditions, minimum energy use
$mix$	regarding mixing process

out	referring to streams out of the process
reb	in reboiler
P	isobaric
SEP	regarding separation process
T-adj	corresponding to temperature adjustment stage
T-demix	corresponding to demixing temperature
V	evaporation

#### Other designations

$\Delta X$	net change of property X
$\bar{X}$	thermodynamically averaged (the temperature, that corresponds to the same entropy flux due to heat exchange, as equal to entropy flux due to heat exchange in range including temperature change of media during the process)
$\dot{X}$	flux (flow) of property
ROL	rectifying operating line
SOL	stripping operating line

#### References

- [1] Agrawal R, Fidkowski ZT. On the use of intermediate reboilers in the rectifying section and condensers in the stripping section of a distillation column. *Ind. Eng Chem Res* 1996;35(8):2801–7. <http://dx.doi.org/10.1021/ie9601312>.
- [2] Agrawal R, Herron DM. Optimal thermodynamic feed conditions for distillation of ideal binary mixtures. *Aiche J* 1997;43(11):2984–96. <http://dx.doi.org/10.1002/aic.690431111>.
- [3] Aguirre P, Espinosa J, Tarifa E, Scenna N. Optimal thermodynamic approximation to reversible distillation by means of interheaters and intercoolers. *Ind. Eng Chem Res* 1997;36(11):4882–93. <http://dx.doi.org/10.1021/ie9608115>.
- [4] Bandyopadhyay S. Effect of feed on optimal thermodynamic performance of a distillation column. *Chem Eng J* 2002;88(1–3):175–86. [http://dx.doi.org/10.1016/S1385-8947\(01\)00303-5](http://dx.doi.org/10.1016/S1385-8947(01)00303-5).
- [5] Bandyopadhyay S, Malik RK, Shenoy UV. Temperature-enthalpy curve for energy targeting of distillation columns. *Comput Chem Eng* 1998;22(12):1733–44. [http://dx.doi.org/10.1016/S0098-1354\(98\)00250-6](http://dx.doi.org/10.1016/S0098-1354(98)00250-6).
- [6] Barbosa D, Doherty MF. The influence of equilibrium chemical reactions on vapor-liquid phase diagrams. *Chem Eng Sci* 1988;43(3):529–40. [http://dx.doi.org/10.1016/0009-2509\(88\)87014-3](http://dx.doi.org/10.1016/0009-2509(88)87014-3).
- [7] Barnicki SD, Hoyme CA, Siirola JJ. Separations process synthesis kirk-othmer encyclopedia of chemical technology. John Wiley & Sons, Inc; 2000.
- [8] Chang HS, Chuang SC. The intrinsic and extrinsic exergy losses of distillation columns. *J Chin Inst Chem Eng* 2001;32(5):469–75.
- [9] Cussler EL, Dutta BK. On separation efficiency. *Aiche J* 2012;58(12):3825–31. <http://dx.doi.org/10.1002/aic.13779>.
- [10] de Koeijer G, Rivero R. Entropy production and exergy loss in experimental distillation columns. *Chem Eng Sci* 2003;58(8):1587–97. [http://dx.doi.org/10.1016/S0009-2509\(02\)00627-9](http://dx.doi.org/10.1016/S0009-2509(02)00627-9).
- [11] Demirel Y. Thermodynamic analysis of separation systems. *Sep Sci Technol* 2004;39(16):3897–942. <http://dx.doi.org/10.1081/ss-200041152>.
- [12] Dimian AC, Bildea CS, Kiss AA. Pinch point analysis. *Computer aided chemical engineering*, vol. 35; 2014. p. 525–64.
- [13] Fonyo Z. Thermodynamic analysis of rectification. 1. Reversible model of rectification. *Int Chem Eng* 1974;14(1):18–27.
- [14] Fonyo Z, Rev E. Energy saving techniques in distillation. In: Bejan A, Mamut E, editors. *Thermodynamic optimization of complex energy systems*, vol. 69; 1999. p. 279–96. NATO Science Series.
- [15] Hernandez AC, Roco JMM, Medina A, Sanchez-Salas N. Heat engines and the Curzon-Ahlborn efficiency. *Rev Mex De Fis* 2014;60(5):384–9.
- [16] Johannessen E, Rosjorde A. Equipartition of entropy production as an approximation to the state of minimum entropy production in diabatic distillation. *Energy* 2007;32(4):467–73. <http://dx.doi.org/10.1016/j.energy.2006.06.009>.
- [17] Kencse H, Mizsey P. Methodology for the design and evaluation of distillation systems: exergy analysis, economic features and GHG emissions. *Aiche J* 2010;56(7):1776–86. <http://dx.doi.org/10.1002/aic.12101>.
- [18] Kiss AA. *Advanced distillation technologies - design, control and applications*. John Wiley & Sons, Ltd; 2013.
- [19] Kiss AA, Infante-Ferreira CA. *Heat pumps in chemical process industry*. CRC-Press, Taylor & Francis Group; 2016.
- [20] Kiss AA, Olujić T. A review on process intensification in internally heat-integrated distillation columns. *Chem Eng Process Process Intensif* 2014;86:125–44.
- [21] Labutin VA, Labutina AV. Calculating the boiling point of a multicomponent liquid-phase mixture. *Theor Found Chem Eng* 2001;35(5):520–2. <http://dx.doi.org/10.1023/A:1012346608719>.
- [22] McCabe WL, Thiele EW. Graphical design of fractionating columns. *Ind. Eng Chem* 1925;17(6):605–11. <http://dx.doi.org/10.1021/ie50186a023>.
- [23] Melpolder FW, Headington CE. Calculation of relative volatility from boiling points. *Ind. Eng Chem* 1947;39(6):763–6. <http://dx.doi.org/10.1021/ie50450a011>.
- [24] Nakaiwa M, Huang K, Endo A, Ohmori T, Akiya T, Takamatsu T. Internally heat-integrated distillation columns: a review. *Chem Eng Res Des* 2003;81(A1):162–77. <http://dx.doi.org/10.1205/026387603321158320>.
- [25] Ognisty TP. Analyze distillation columns with thermodynamics. *Chem Eng Prog* 1995;91(2):40–6.
- [26] Opfell JB. Free-energy explanation of separative work. *Aiche J* 1978;24(4):726–8. <http://dx.doi.org/10.1002/aic.690240423>.
- [27] Ravi R. A rigorous analysis of McCabe-Thiele assumptions and their consequences: critical role of parallel enthalpy lines. *Chem Eng Commun* 2006;193(1):55–68. <http://dx.doi.org/10.1080/009864490923493>.
- [28] Reddy CCS, Fang Y, Rangaiah GP. Improving energy efficiency of distillation using heat pump assisted columns. *Asia-Pac J Chem Eng* 2014;9(6):905–28. <http://dx.doi.org/10.1002/apj.1842>.
- [29] Richterova V. Application of heat-pump in rectification decreases energy-consumption in the chemical-industry. *Energy Convers Manag* 1991;32(6):519–28. [http://dx.doi.org/10.1016/0196-8904\(91\)90111-u](http://dx.doi.org/10.1016/0196-8904(91)90111-u).
- [30] Shiras R, Hanson D, Gibson C. Calculation of minimum reflux in distillation columns. *Ind. Eng Chem* 1950;42(5):871–6.
- [31] Wei ZQ, Zhang BJ, Wu SY, Chen QL, Tsatsaronis G. Energy-use analysis and evaluation of distillation systems through avoidable exergy destruction and investment costs. *Energy* 2012;42(1):424–33. <http://dx.doi.org/10.1016/j.energy.2012.03.026>.
- [32] Zemp RJ, deFaria SHB, Maia M. Driving force distribution and exergy loss in the thermodynamic analysis of distillation columns. *Comput Chem Eng* 1997;21:S523–8. [http://dx.doi.org/10.1016/S0098-1354\(97\)87555-2](http://dx.doi.org/10.1016/S0098-1354(97)87555-2).