

Integrated Column Designs for Minimum Energy and Entropy Requirements in Multicomponent Distillation

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Abstract

In the evaluation of minimum energy consumption (1st law) we here also discuss minimum entropy production, or lost work (2nd law). This leads us to the reversible Petlyuk arrangement. However the total required heat supply is higher in this case than for the typical (adiabatic) Petlyuk arrangements, but there is a potential for further reduction by use of internal heat integration. This principle can also be applied to general arrangements (not only reversible) and we compare set of alternative distillation arrangements for a given feed example. We also conjecture that the generalized extended adiabatic (not reversible) Petlyuk arrangement require less energy than any other adiabatic arrangement at constant pressure when we consider configurations without internal heat integration.

1 Introduction

What is the minimum energy requirement for separating a given multicomponent mixture by distillation? This is a fundamental question of significant practical importance, yet it remains unsolved even for the case of ideal mixtures, at least when we consider the practical case with adiabatic column sections. However, we conjecture that, with constant pressure and without internal heat integration, the generalized extended adiabatic (not reversible) Petlyuk arrangement requires less energy than any other adiabatic arrangement. The energy requirement is then easily computed as the being equal to the most difficult binary split (Halvorsen 2001). The minimum energy requirement when we allow for internal heat exchange remains unknown.

However, minimum energy (1st law) is by itself not sufficient as a measure, because also the quality (temperature) of the energy matters. Specifically, we prefer a process where the energy may be supplied at a low temperature and cooling may be supplied at a high temperature. To take this into account, we also consider the entropy production or lost work (2nd law).

This leads us to the reversible Petlyuk arrangement described by Grunberg (1956), Petlyuk et. al. (1964 and 1965) and Fonyó (1974ab). An overview is also found in the textbook by King (1980). A characteristic of the *reversible distillation* column is that some of the heat is supplied continuously along the bottom (stripping) sections and removed along the top (rectifying) sections.

We here consider the separation of ideal mixtures for which we may assume constant relative volatility and constant molar flows and for the entropy calculations we also assume equal heat of vaporization and negligible liquid volume compared to the gas volume. We assume infinite number of stages because this provides a lower bound on the energy requirement for ideal mixtures. In practice with a finite number of stages, the actual energy requirement may be about 10% higher. With these simplifying assumptions, analytic expressions for minimum energy and for the relative entropy production have been derived for several important distillation configurations (Halvorsen 2001). A review of the expressions are given in Section 3.

2 Example

To illustrate the results we consider the energy requirement, given in terms of the total produced vapour rate V/F and the entropy production, given in terms of the relative entropy production $S_r = \Delta S_{total}/\Delta S$ where ΔS is the entropy of mixing for a specific case, and ΔS_{total} is the total entropy production when a particular process is applied. For a reversible process, the second law of thermodynamics states that $\Delta S_{total} = 0$.

The considered configurations are shown in Figures 1, 2 and 3. We use an equimolar saturated liquid ternary feed with constant relative volatility ($\alpha = [4, 2, 1]$) between the components A, B and C). Figure 1 shows two-column configurations where one of the feed components is separated as a pure product in the first column. Figure 2 and 3 show prefractionator

arrangements, where the first column performs a sharp A/C split while the intermediate B is distributing to both products. Figure 3 shows prefractionator arrangements with internal heat integration. The results are briefly discussed below and are summarized in Table 1.

Let us first consider the conventional “direct split” arrangement with two two-product columns (Figure 1a). Here we take in the first column A as the top product and the remaining mixture of B/C as the bottom product. The second column separates B and C, and we get B in the top and C in the bottom. The total energy requirements in the two column reboilers is $V/F=2.072$ and the entropy production is $S_r=0.59$. Some energy reduction may be achieved with the “indirect split” (Figure 1b) where we in the first column take C as the bottom product and A/B as a vapour top product. The second column separates A and B. Here $V/F=2.032$, but the entropy production is higher, $S_r=1.21$, because the temperature difference between heat supply and cooling is larger. The directly coupled side rectifier and side stripper performs better in terms of minimum energy (both have $V/F=1.882$), but the direct split configuration has still lower entropy production (Table 1).

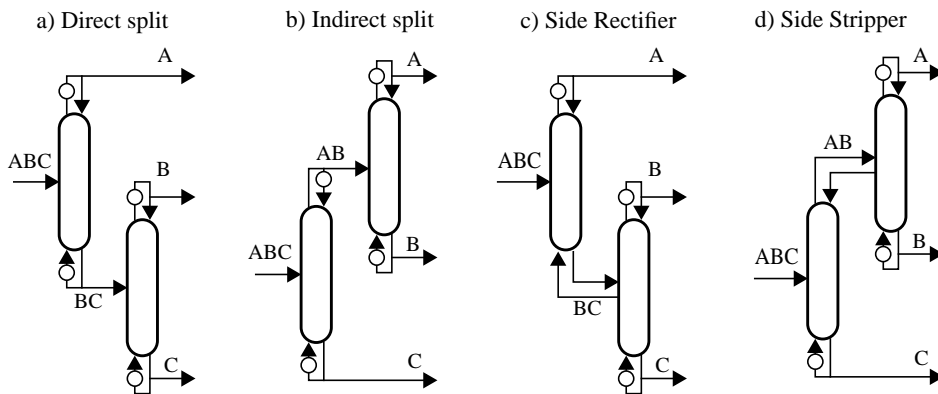


Figure 1: Conventional two-column configurations for separation of ternary mixtures. No internal heat integration is applied.

The fully reversible arrangement shown in Figure 2a is ideal in terms of entropy production ($S_r=0.0$), but the total amount of heat supplied in the reboiler and along the bottom sections of the three internal columns ($V/F=1.667$) is higher than for the other prefractionator arrangements in Figure 2. However, much of the heat is supplied at lower temperatures. The conventional prefractionator arrangement in Figure 2b is also interesting since it may approach the Petlyuk column in terms of minimum energy ($V/F=1.556$) and the entropy production, ($S_r=0.63$) is approaching the direct split.

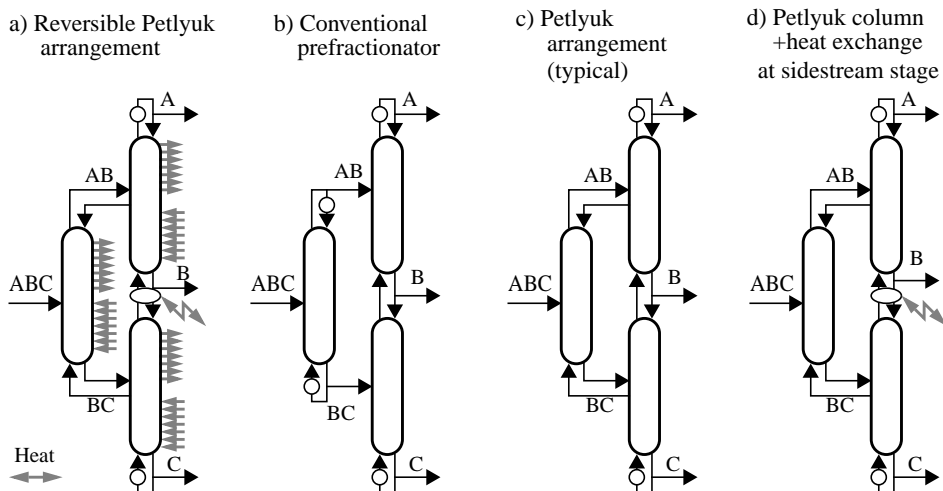


Figure 2: Prefractionator arrangements (three two-product columns) for separation of ternary mixtures. No internal heat integration.

The adiabatic directly coupled Petlyuk column with a single reboiler as shown in Figure 2c achieves $V/F=1.366$. This is more than 30% energy reduction compared to the conventional direct split configuration and the Petlyuk column is the best adiabatic arrangement in terms of energy (Halvorsen 2001). However, the entropy production remains high, $S_r=0.72$, because all the heat is supplied at the highest temperature (boiling point of component C) and all the cooling is at the lowest temperature (boiling point of component A). However, in this case, the vapour requirement above the sidestream is lower than below, so we may take out some heat at the intermediate boiling point (component B) by condensing some vapour at the sidestream stage and thereby reduce the entropy production to $S_r=0.54$. Thus, the modified Petlyuk arrangement in Figure 2d performs better than the direct split configuration (Figure 1a) also in terms of entropy production. To further reduce the energy requirements we must allow for internal heat exchange. For example (Figure 3b), for this specific mixture we may in the Petlyuk column preheat the feed with the sidestream product and achieve $V/F=1.181$ and $S_r=0.49$.

To significantly reduce the energy consumption further we must allow for non-adiabatic sections with continuous heat exchange. For example, for this specific mixture, if we allow for heat exchange between the middle four sections in the Petlyuk column (Figure 2c), then we may achieve $V/F=1.000$ and $S_r=0.26$. A practical case which is more realistic is a Dividing Wall Column (DWC) where we allow heat exchange across the dividing wall (equivalent to Figure 3a). In the given example, heat transfer below the sidestream is achievable and with ideal heat transfer the vapour supply can be reduced to $V/F=1.22$ but with $S_r=0.54$. Lestak et al. (1994) considered heat transfer across the wall for a given case, and it was found that it could be beneficial to allow for heat transfer along a part of the dividing wall and insulate the other part. But the overall reduction in heat input was found to be small.

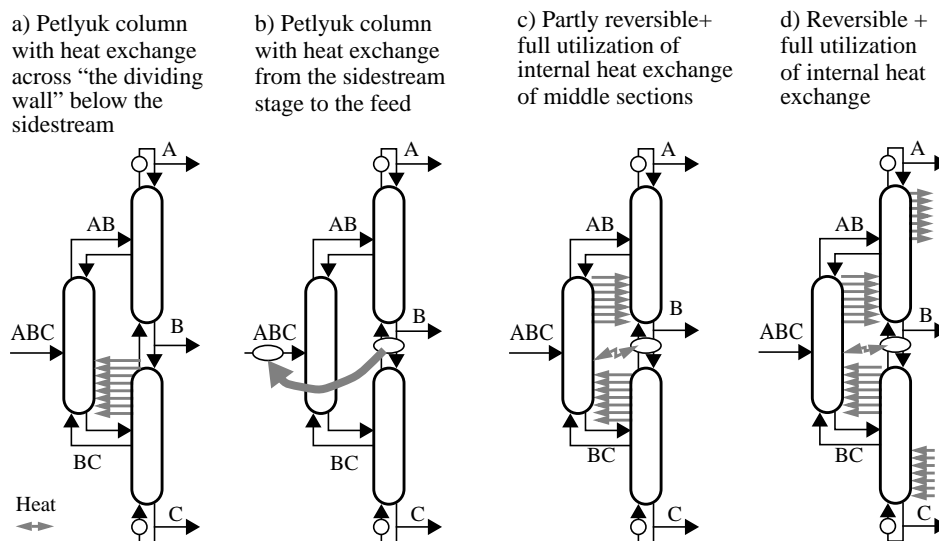


Figure 3: Directly coupled ternary arrangements where internal heat integration is used to reduce both external heat supply and loss of separation work.

To achieve further reductions let us again consider the reversible distillation process in Figure 2a where the entropy production is zero, $S_r=0$. We may introduce internal heat pumps (not shown) so that all external heat supply is at the highest temperature. In this way we may reduce the energy requirement to $V/F=0.793$, which is the theoretical minimum for the separation of this mixture by distillation at constant pressure.

3 Minimum Energy and Entropy Calculations

A set of expressions for entropy and minimum energy calculations have been derived in Halvorsen (2001) and the most important equations used in the above example are presented below. The term *adiabatic column* section, as used by Petlyuk et. al. (1964), denote a column section with constant molar flows and no heat exchange along the section. In *non-adiabatic sections* we can supply or remove heat continuously at any stage in the section. A *reversible section* is an infinite non-adiabatic section where the heat is supplied or removed in a way that eliminates mixing irreversibility between neighbouring stages. In a *column arrangement* we put together a number of sections, reboilers and condensers. Sections may be *directly (fully thermally) coupled*, by two-way liquid and vapour streams or may be coupled via condensers or reboilers. The *Minimum energy* is the minimum required external heat supply to reboilers and to non-adiabatic column sections. We use the total requirement for *vaporization* or *vapour flow* as a measure of the energy requirement.

Table 1: Comparison of minimum energy (external heat supply) and relative entropy production (lost work) for a set of column arrangements for a given feed. The list is sorted by descending minimum energy.

Figure	Configuration (Ad: Adiabatic Non: Non-ad.)	Energy (V_{min})	Entropy (S_r)
1a	Direct Split (conventional)	Ad	2.072
1b	Indirect Split (conventional)	Ad	2.032
1c	Side Rectifier (directly coupled)	Ad	1.882
1d	Side Stripper (directly coupled)	Ad	1.882
2a	Reversible Petlyuk Column	Non	1.667
2b	Separate prefractionator arrangement	Ad	1.556
2c	Petlyuk Column (minimum energy without internal heat exchange)	Ad	1.366
2d	Petlyuk Column with heat removal or supply at sidestream stage	Ad	1.366
3a	Petlyuk column with heat exchange across the dividing wall	Ad+Non	1.222
3b	Petlyuk column with heat exchange from sidestream to feed	Ad	1.181
3c	Petlyuk with total heat exchange in middle sections	Ad+Non	1.000
3d	Reversible Petlyuk column with internal heat exchange	Non	1.000
-	Reversible process with only two temperature levels (The theoretical minimum energy process)	Non	0.793

3.1 Entropy Production (2nd law)

The entropy change (ΔS) when mixing N_c pure compounds at constant pressure and temperature is given by (x denotes mole fraction):

$$\Delta S = R \sum_{i=1}^{N_c} x_i \ln(x_i) \quad (1)$$

The entropy change in the surroundings (ΔS_{sur}) depends on the actual process, and can be calculated from:

$$\Delta S_{sur} = -\oint \frac{dQ}{T} \text{ or } \Delta S_{sur} = -\sum_j \frac{Q_j}{T_j} \quad (2)$$

where dQ (is the actual heat transferred at system temperature T . The integral has to be taken around the system boundaries where heat transfer to the surroundings occur. The second expression is used when the heat is supplied or removed at discrete temperature levels (Q_j at T_j), for example in a reboiler and a condenser. If we can find a process where the total entropy change ($\Delta S_{total} = \Delta S_{sur} + \Delta S$) is zero (or $\Delta S_{sur} = -\Delta S$), it is reversible. A normalized measure of entropy production is given by the *relative entropy production*, defined here as:

$$S_r = \frac{\Delta S_{total}}{|\Delta S|} = \frac{\Delta S_{sur} + \Delta S}{|\Delta S|} \quad (3)$$

It can be shown (Halvorsen 2001) that with the simplifying assumptions used in this paper, the temperature-composition-pressure relationship (T - x - P) for a multicomponent mixture (see also Petlyuk (1964) for a binary mixture) is given by:

$$\frac{1}{T} = \frac{R}{\lambda} \ln \left(\frac{P_{ref}}{P} \sum_i \alpha_i x_i \right) + \frac{1}{T_{b,r}} \quad (4)$$

Here $T_{b,r}$ is the boiling point for the reference component at the reference pressure P_{ref} , λ is the molar heat of vaporization, which is assumed equal for all components, and the universal gas constant $R=8.31 [JK^{-1}mol^{-1}]$.

Now we consider a column (or just a section) with constant vapour flow (V) and known composition and pressure in the top (T) and bottom (B). Then equation (2) combined with (4) gives:

$$\Delta S_{sur} = \lambda V \left(\frac{1}{T_T} - \frac{1}{T_B} \right) = RV \ln \left(\frac{\sum (\alpha_i^{x_i, T}) P_B}{\sum (\alpha_i^{x_i, B}) P_T} \right) \quad (5)$$

Note that this expression is independent of the heat of vaporization, the boiling point temperatures and the absolute pressure. In the case of constant pressure and sharp separation between a binary mixture of components L and H , (5) is simplified to:

$$\Delta S_{sur} = RV \ln \alpha_{LH} \quad (6)$$

The entropy production in adiabatic Petlyuk arrangements can also be found by the expression for single adiabatic sections. For the ternary case (Figure 2c or d), given by the vapour flows and temperatures in the reboiler (B) condenser (T) and the sidestream stage (S), we obtain from (5):

$$\Delta S_{sur} = \lambda \left(V_B \left(\frac{1}{T_S} - \frac{1}{T_B} \right) + V_T \left(\frac{1}{T_T} - \frac{1}{T_S} \right) \right) = \lambda R (V_B \ln \alpha_{BC} + V_T \ln \alpha_{AB}) \quad (7)$$

In the typical Petlyuk arrangement (Figure 2c) the vapour flow is constant through the arrangement and: $\Delta S_{sur} = RV \ln \alpha_{AC}$ (where $\ln \alpha_{AC} = \ln \alpha_{BC} + \ln \alpha_{AB}$). Note that ΔS_{sur} (or S_r) is always lower for the modified arrangement with possibilities to supply or remove heat at the sidestream stage (Figure 2d).

3.2 Minimum Energy (1st law)

Even though the net heat supply is zero ($\oint dQ = 0$) it is useful to distinguish between heating ($dQ > 0$) and cooling ($dQ < 0$). We write $dQ = dQ_H + dQ_C$, where the heating $dQ_H = \max(dQ, 0)$ and cooling $dQ_C = \min(dQ, 0)$. Note that the total heat supply equals the total cooling and is given by:

$$Q_H = \oint dQ_H = -Q_C = -\oint dQ_C \quad (8)$$

This is a useful measure from an energy point of view (1st law). Ideally we want to have both ΔS_{total} small (small lost work, i.e. good 2nd law performance) and Q_H small (small total heat supply, i.e. good 1st law performance). The ideal separation process with a minimum value of Q_H is a reversible process with all the heating at the highest temperature (T_H) and all the cooling at the lowest temperature (T_L). The vaporization rate (V) is related to the heat by $Q_H = \lambda V$. For an ideal reversible process working between two temperature levels we obtain we from (2):

$$V_{rev, min} = \frac{Q_{Hmin}}{\lambda} = \frac{-\Delta S}{\lambda \left(\frac{1}{T_L} - \frac{1}{T_H} \right)} = \frac{-\Delta S/R}{\ln \alpha_{LH} + \ln \frac{P_H}{P_L}} \quad (9)$$

Note that for constant pressure and sharp binary split, the relative volatility is the only required physical property.

3.3 Minimum Energy of Extended Petlyuk Arrangements

For the generalized adiabatic Petlyuk arrangement Halvorsen (2001) showed that the minimum energy requirement for separation of a feed mixture of N_c components into N_c pure products is given by:

$$V_{min}^{Petlyuk} = \max_j \sum_{i=1}^j \left(\frac{\alpha_i z_i F}{\alpha_i - \theta_j} \right), \text{ where } j \in \{1, N_c - 1\} \quad (10)$$

Note that this is the same as the most difficult binary split in a two-product column. Here θ_i are the $N_c - 1$ common Underwood roots (Underwood 1948) found from (q is liquid fraction in the feed (F) and z is the feed composition):

$$\sum_i \frac{\alpha_i z_i}{\alpha_i - \theta} = 1 - q \quad (11)$$

It has been conjectured (Halvorsen 2001) that the adiabatic Petlyuk arrangement, where all the heat is supplied in the bottom reboiler at the maximum temperature, requires minimum energy (V_{min}) compared to any other adiabatic distillation arrangement (without internal heat exchange). However, no proof has been found in the literature (Petlyuk 2000), except for the

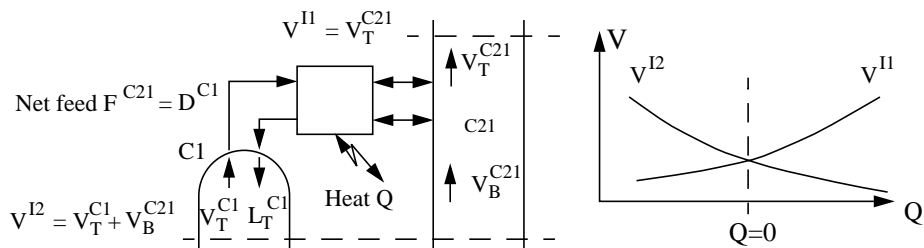


Figure 4: General column interconnection junction. The direct (full thermal) coupling gives $\min(\max(V^{I1}, V^{I2}))$ for zero external heat exchange at the interconnection ($Q=0$).

ternary case (Fidkowski and Krolikowski 1987). Figure 4 illustrates the result from Halvorsen (2001) that the direct (full thermal) coupling minimize the total vapour flow through the cross-sections above or below a column junction. Thus by replacing any junction with something else than a direct coupling, the vapour requirement has to increase somewhere in the arrangement. However, this is a conjecture since it has not been generally shown for all possible column arrangements.

4 Conclusion

Reversible distillation gives valuable insight in the energy requirement for multicomponent distillation. However, even if the reversible arrangement is optimal with respect to entropy production or lost work (2nd law), we may have irreversible (adiabatic) systems with less energy consumption (1st law). Without considering any internal heat exchange, the adiabatic Petlyuk arrangement seems to achieve less minimum energy requirement than any other distillation system.

Internal heat exchange can be used for further reduction of the minimum external energy (heat supply). Heat exchange can be applied in any system where the temperature ranges where we need heat supply overlaps temperature ranges where heat is available. Thus, it can be applied for the ideal reversible arrangement as well as for the adiabatic Petlyuk column and also for conventional column arrangements. With a given total temperature range, the minimum energy target can be defined by a theoretical reversible distillation process where all the energy is supplied at the highest temperature and removed at the lowest temperature.

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