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Minimizing Entropy Production Rate in Binary Tray Distillation*

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Abstract

In this work we increase the second law efficiency in an ideal binary tray distillation column by allowing heat exchangers on all trays. We find by numerical optimization, the duties of the heat exchangers that gives the highest second law efficiency of the column. The entropy production rate was reduced by 30-50% compared to adiabatic operation for two different columns. The numerical optimum was in agreement with the result of an Euler-Lagrange minimization in which the total entropy production rate was described by irreversible thermodynamics. The minimum was not characterized by equipartition of forces.

Key words: Distillation, minimum entropy production rate, irreversible thermodynamics

1. Introduction

Distillation is widely used in the process industry despite its low second law efficiency (5-20%). We have studied the addition of heat exchangers on the trays as a way to increase the efficiency in ideal binary tray distillation, that is diabatic distillation, see Rivero (1995) and le Goff et al. (1996). In this work we allow heat exchangers on all trays. The aim of the work is to find the variation of the duties of these exchangers across the column (called duty profile) that gives the minimum entropy production rate. A numerical method will be compared with an analytical method based on irreversible thermodynamics. We optimize two different example columns that perform a given separation, i.e. the same amounts and mole fractions in the distillate and bottom. Another objective is to compare the solutions of the methods with the principle of equipartition of forces. This principle says that the force is constant on each tray in the case of minimum entropy production, see Sauar (1998), Ratkje et al. (1995). It is known that this solution is not true if the number of constraints on the minimization is increased beyond that of constant production (amount of transferred mass), see Bedeaux et al. (1999). Sauar (1998) and coworkers also found limitations to the principle of equipartition of forces.

2. The system

The binary tray distillation column has heat exchangers on all trays. We calculate the entropy production rate due to heat and mass transport through the liquid-gas interface on each tray, see Eq. 1 below. The entropy production rate due to the temperature difference between the in- and outlet of the cooling and heating media is not taken into account at this stage.

TABLE I. COLUMN PARAMETERS

	Alkane	Alcohol
Component 1	n-pentane	methanol
Component 2	n-heptane	isopropyl-alcohol
Pressure(bar)	1.00	0.75
Feed(mol/s)	100	100
Distillate(mol/s)	26.531	48.913
Bottom(mol/s)	73.469	51.087
x_1^F	0.270	0.500
x_1^D	0.990	0.970
x_1^B	0.010	0.050
Trays	15	19
Feed tray	8	10

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The column is defined by the pressure, feed flow (F), distillate flow (D), number of trays (N), feed tray location, mole fractions in the feed (x_i^F), and the mole fractions in the distillate (x_i^D), see TABLE I. Mass balances then gives the bottom flow (B) and the mole fractions in the bottom (x_i^B). These parameters are also given in the table. The reboiler and condenser are the first and last tray, respectively. The feed tray is the one which gives minimum entropy production rate in the adiabatic column.

3. Theory

3.1. Three flows and their corresponding forces

Figure 1 illustrates the details of the processes on a tray. The flows and mole fractions below tray number n have subscript n; the flows and mole fractions above tray number n have subscript n+1.

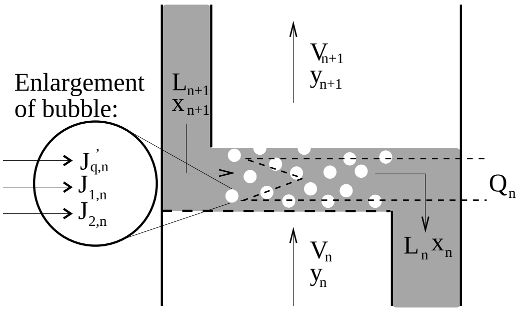

Figure 1. Schematic representation of a tray

The flow of component i on tray n, $J_{i,n}$, is the flux times the area of transfer. This area is assumed to be constant during the equilibration process on the trays. The entropy production rate for tray number n is then (de Koeijer et al. (1999)):

$$\begin{aligned} \Delta S_n^{prod} &= J'_{q,n}\Delta_n\left(\frac{1}{T}\right) - J_{1,n}\frac{1}{T_n}\Delta_n\mu_{1,T} - \\ & J_{2,n}\frac{1}{T_n}\Delta_n\mu_{2,T} \end{aligned} \quad (1)$$

The flows are the flows of measurable heat ($J'_{q,n}$) and mass ($J_{i,n}$) from the liquid into the gas phase. The forces for mass transport($-\frac{1}{T_n}\Delta_n\mu_{i,T}$) and heat transport($\Delta_n\left(\frac{1}{T}\right)$) are obtained by integrating between the vapor in- and outlets of tray *n* (with the assumption of a constant averaged flow during the equilibration process). In terms of vapor mole fractions (y) we have for the force for mass transport:

$$X_{i,n} = -\frac{1}{T_n}\Delta_n\mu_{i,T} = -R\ln\frac{y_{i,n+1}}{y_{i,n}} \quad (2)$$

In the integration, it is assumed that the process ends when there is equilibrium on the tray. The assumptions behind Eq.1, are not correct on a molecular level, but provide a good approximation for this work.

3.2. The entropy production rate in reduced form

The expression 1 is still complicated, and a simplified version is sought. Our experience so far in Ratkje et al. (1995), de Koeijer et al. (1999) is that the thermal force and flow gives a small contribution to the entropy production (<8%). We shall therefore neglect the first term to the right in Eq.1. The two remaining terms are related by the Gibbs-Duhem equation. We shall use:

$$\begin{aligned} -\bar{y}_n\Delta\mu_{1,T}^{vap} &= \Delta\mu_{2,T}^{vap} \\ \text{where} \quad \bar{y}_n &= \sqrt{\frac{y_{1,n}y_{1,n+1}}{y_{2,n}y_{2,n+1}}} \end{aligned} \quad (3)$$

By integrating only over variations in the vapor phase, we have assumed that the entropy production rate in the system is in the vapor, and/or at the boundary between gas and liquid. The reduction of the entropy production rate to a one flow - one force expression is now possible:

$$\begin{aligned} \Delta S_n^{prod} &= (-J_{1,n} + \bar{y}_n J_{2,n})\frac{1}{T_n}\Delta\mu_{1,T} \\ &= J_n^{tot}X_{1,n} \end{aligned} \quad (4)$$

Better approximations for the flows and forces than these may be found when phenomenological coefficients become available (Bedeaux et al. (1999)), and we do not longer need the assumption of equilibrium between liquid and vapor at the outlets on all trays. The entropy production rate on a tray can be calculated from Eq. 4, but also from the entropy balance on each tray:

$$\begin{aligned} \Delta S_n^{prod} &= V_n S_n^{vap} + L_{n+1}S_{n+1}^{liq} \\ & -V_{n+1}S_{n+1}^{vap} - L_n S_n^{liq} + \frac{Q_n}{T_n} \end{aligned} \quad (5)$$

The entropies (S) are given by an equation of state, and Q_n is the heat added from the heat exchanger at tray n and temperature T_n. We shall use Eq.5 to evaluate Eq.4.

3.3. Euler-Lagrange minimization

The minimum value of the entropy production rate in Eq. 4 is pursued, given the boundary conditions listed in TABLE I. The minimization problem can be formulated as

Biegler et al. (1997):

$$\begin{aligned}
\text{min} \quad & \textstyle\sum_1^N \Delta S_n^{prod} = \sum_1^N J_n^{tot} X_{1,n} \\
\text{s.t.} \quad & F x_1^F - B x_1^B = D x_1^D = \textstyle\sum_1^N J_{1,n} = I_1 \\
& F x_2^F - B x_2^B = D x_2^D = \textstyle\sum_1^N J_{2,n} = I_2 \\
& R \ln\left(\frac{x_1^D}{x_1^B}\right) = \textstyle\sum_1^N X_{1,n} = I_3 \\
& R \ln\left(\frac{x_2^D}{x_2^B}\right) = \textstyle\sum_1^N X_{2,n} = I_4 \qquad (6)
\end{aligned}$$

The two constraints on the flows, with values I_1 and I_2, represent the productions (or transferred amounts of mass) of the two components. The last two constraints, I_3 and I_4, fix the energy levels of the output flows (the chemical potentials of the two components). The four constraints are independent of one another. By working out Eq. 6, we obtain:

$$\begin{aligned}
2J_n^{tot} &= -\lambda_1 \ell_{1,n} - \lambda_2 \ell_{2,n} - \lambda_3 + \lambda_4 \bar{y}_n \\
&\text{where} \quad \ell_{i,n} = \frac{J_{i,n}}{X_{1,n}} \qquad (7)
\end{aligned}$$

The λ's are the Lagrange multipliers. The result does not depend on the variable chosen for the minimization ($X_{1,n}$, $X_{2,n}$, $J_{1,n}$, $J_{2,n}$ or J_n^{tot}). The minimum entropy production rate should be characterized by Eq. 7. The equation means that we neither have a uniform distribution of forces, nor of entropy production.

4. Calculation procedure

The tray column simulation method described earlier de Koeijer et al. (1999) gave mole fraction -, flow -, and temperature profiles. Entropies were obtained from the Peng-Robinson equation of state. The entropy production was calculated according to Eqs. 4 and 5. A minimization algorithm was constructed, called a bouncing algorithm, containing a random and a deterministic part. The numbers given in the following are illustrative. To start, a duty profile was chosen that did not violate mass and/or energy balances. The randomization part consisted of the generation of a new profile by a random stepwise increase or decrease of the duty on one random tray. The new duty profile was simulated accordingly. In the cases that the entropy production rate became higher or that the mass- and/or energy balances were violated, the new duty profile was rejected, and a new random step was made from the previous duty profile. In the case that the entropy production rate became smaller, the new duty profile was accepted as a new starting point. As the deterministic element the random step was multiplied by an exponentially decreasing factor f. In this way the entropy production rate decreased to a minimum. To bounce out of a possible local minimum, the entropy production rate was multiplied by a factor 1.5 and the procedure repeated 1000 times, starting with a high value for the factor f. In this way the entropy production can bounce out of a local minimum and hopefully end up bouncing around the global minimum. We cannot prove that this numerical procedure guarantees a global minimum. On the other hand, we were able to reproduce the results by repeating the procedure, with different starting points and algorithm parameters. Also the bouncing in and out of local minima could be observed.

5. Results and discussion

5.1. Consistency of data sets

The entropy production rate was calculated from Eq. 4 and plotted as a function of the entropy production rate from Eq. 5 for all trays in the adiabatic as well as the diabatic columns. *Figure 2* gives the results for the pentane-heptane column and *Figure 3* gives the same for the methanol-isopropylalcohol column . Each point in the figures represents one tray. We see that there is good consistency between results from the two equations for both columns with minimum entropy production rate, see the dark points in both figures. Only for the adiabatic column that separates alkanes, the consistency was less good. The consistency is overall remarkable, considering the number of assumptions that we have used. Model errors in the Peng-Robinson equation of state may also contribute to the deviations.

5.2. The duty and temperature profiles from the numerical minimization procedure

The results of the numerical minimization are given in *Figure 5* for the alcohol column and in *Figure 4* for the alkane column. The duty profile in the corresponding adiabatic columns are also given in the figures. The heat exchanger at tray number 1 is the reboiler and the heat exchanger at the tray number 15 (alkane column) or 19 (alcohol column) is the condenser. The total entropy production rate in the alkane column was reduced with 47% (from 295.3 to 156.4 J/s K) and in the alcohol column with 29% (from 425.1 to 300.8 J/s K) by applying the given duty profiles. The adiabatic columns have a large positive heat supply in the reboiler, and a large negative heat supply (i.e. a heat release) in the condenser. Otherwise the duties on the trays are zero, as required by the definition of an adiabatic column. The diabatic columns with minimum entropy production rate have the highest positive duties in the reboiler, next to the reboiler and below the feed tray. The highest negative duties are in the condenser, next to the condenser, and above the feed tray.

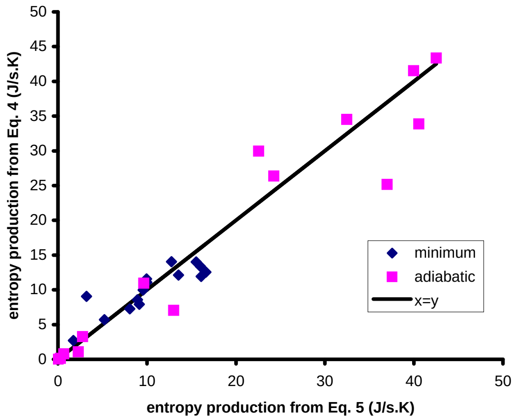

Figure 2. The entropy production rates by alkane separation of Eqs. 4 and 5

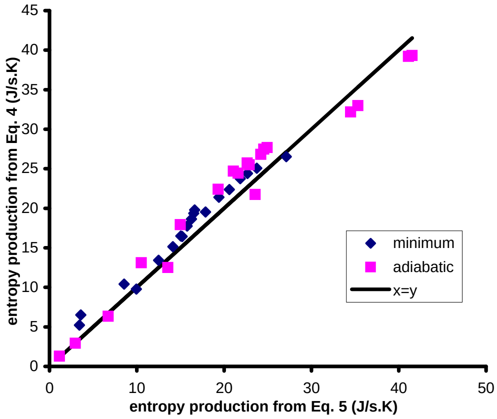

Figure 3. The entropy production rates by alcohol separation of Eqs. 4 and 5

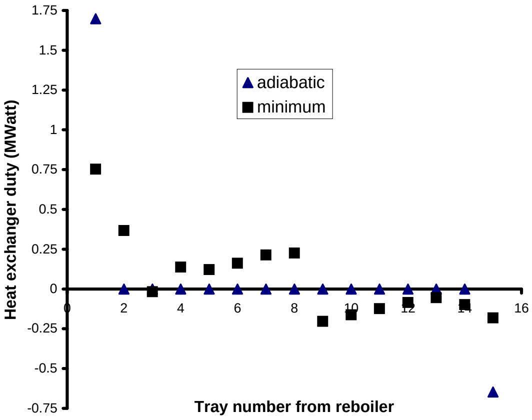

Figure 4. Duty profiles of the alkane separating columns

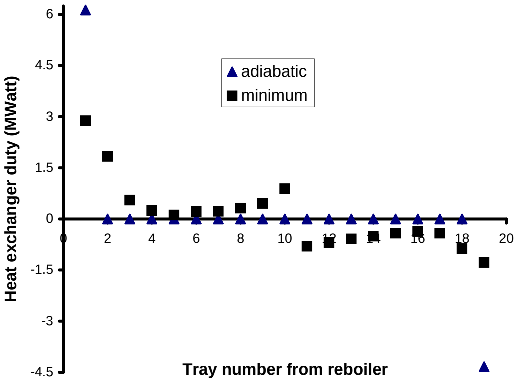

Figure 5. Duty profiles of the alcohol separating columns

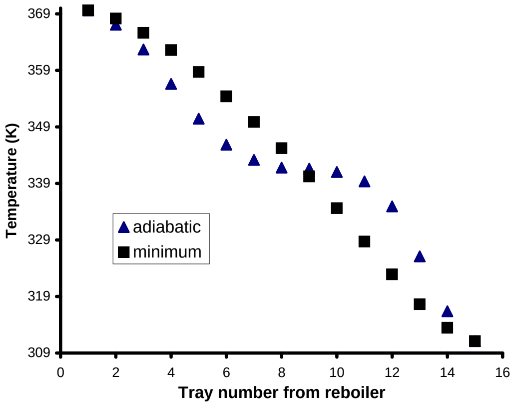

Figure 6. Temperature profiles of the alkane separating columns

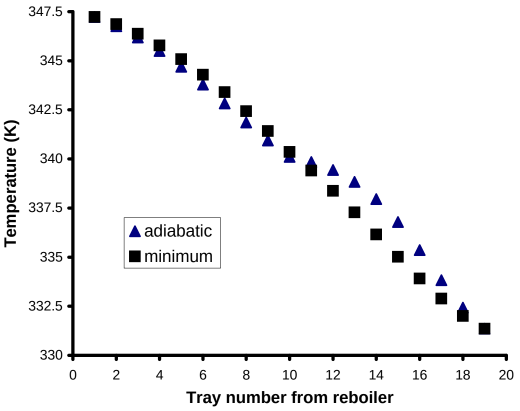

Figure 7. Temperature profiles of the alcohol separating columns

The corresponding temperature profiles are given in *Figure 6* and *7*. The first observation is that the profiles of the columns with minimum entropy production rate are straighter. Secondly, in both profiles the differences between adiabatic and minimum columns are smaller for alcohol separation than for alkane separation (compare Figures 4 and 6 with 5 and 7). This explains the different relative savings on entropy production rate in the two columns. The absolute values of the duties and temperatures given here depend on parameters in TABLE I.

5.3. Comparison of the Lagrange and numerical minimization procedure

The results from*Figures 4, 5, 6,* and*7* were fitted to Eq. 7 using multi-variable linear regression. The resulting Lagrange multipliers and their standard errors are given in TABLES II and III.

TABLE II. LAGRANGE MULTIPLIERS OF THE MINIMUM ENTROPY PRODUCING ALKANE COLUMN

	referring to		unit
λ_1	$\ell_{1,n}$	-1.26±0.11	J/mol K
λ_2	$\ell_{2,n}$	3.08±0.24	J/mol K
λ_3	intercept	-5.64±0.73	mol/s
λ_4	$\overline{y}_n$	1.56±0.098	mol/s

TABLE III. LAGRANGE MULTIPLIERS OF THE MINIMUM ENTROPY PRODUCING ALCOHOL COLUMN

	referring to		unit
λ_1	$\ell_{1,n}$	-0.734±0.063	J/mol K
λ_2	$\ell_{2,n}$	1.20±0.10	J/mol K
λ_3	intercept	-17.8±1.6	mol/s
λ_4	$\overline{y}_n$	7.06±0.53	mol/s

The tables show that Eq. 7 reproduces the results well. The regression coefficients for the fit were 0.995 for the alkane separating column and 0.989 for the alcohol separating column, and rather straight normal probability plots were observed. The data for the adiabatic columns did not show compliance with equation 7. It was observed that the compliance increased with decreasing entropy production rate. The signs of the Lagrange multipliers seem likely. The two components are transferred through the phase boundary in opposite directions. The Lagrange multipliers of the forces and flows, should therefore have opposite signs for the two components, which is indeed observed. We conclude that Eq. 7 is a good model for the minimum entropy production rate of these two binary distillation columns. Mathematical expressions for the Lagrange multipliers are now lacking. Such expressions will make the theory independent of the numerical minimization. A more quantitative analysis of the entropy production rate is required before industry can use the results. We have neglected the contribution of the cooling/heating media in the heat exchangers to the entropy production of the total column. This is most probably a non-negligible contribution.

5.4. Comparison with isoforce operation

For a column with minimum entropy production, Sauar (1998) and Ratkje et al. (1995) have derived the principle of equipartition of forces using only the first two constraints given above in Eq. 6. The operating path of the column was then given by an equal distribution of the forces (isoforce operation). The in- and output mole fractions were not restricted. The literature on this principle supported that this operation was possible Sauar et al. (1997), but Sauar (1998) observed also limitations. Mass balances appeared to be violated in the upper part of a column. We conclude that in general binary diabatic distillation with fixed separation has not enough freedom to adjust to isoforce operation. To come closer to isoforce operation, the designer must be willing to remove the constraints on the forces and to restrict only the amounts of transported mass. A design measure to get the forces more equal on each tray might be to feed on each tray, in addition to the heat exchangers. This might solve the observed mass balance violations. The importance of this work lies more in the method than in the obtained results. Numerical minimization methods, like the bouncing algorithm used here, provide the minimum value of the entropy production rate, but no theoretical basis for it. Our work aims to give such a basis, by investigating the nature of minimum entropy production rate. Systematic efforts should be made to characterize column boundary conditions, that are compatible with minimum entropy production rate. Diabatic distillation is a well known method to reduce entropy production rate, see Rivero (1995). But isoforce operation represents a minimum in entropy production rate that need more degrees of freedom in design than offered by diabatic distillation. It is important to understand the minimum entropy production rate in a diabatic column. But it is also important to find boundary conditions that give isoforce operation, because this operation has yet a lower minimum entropy production rate.

6. Conclusion

A numerical method has been demonstrated that finds the state of minimum entropy production rate in distillation columns with heat exchangers on all trays. The method gives results that are consistent with a theoretical description, based on irreversible thermodynamics and the Euler-Lagrange method. For diabatic distillation with fixed separation it is required that also in- and output energy levels are constraints in the Euler-Lagrange variation. The calculation was simplified with sufficient accuracy, when the entropy production rate was described with only one force and one flow. Future work is now to include the contribution of the heat exchangers into the theoretical minimization, and to a priori determine the values of the Lagrange multipliers.

Acknowledgment

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Nomenclature

B	Bottom (mol/s)
D	Distillate (mol/s)
F	Feed (mol/s)
I	Value of constraint(mol/s or J/mol K)
J	Flow (mol/s or J/s)
L	Liquid flow(mol/s)
N	Number of Trays(-)
Q	Duty(J/s)
R	Gas constant(J/mol K)
S	Entropy (J/mol K)
T	Temperature (K)
V	Vapor flow(mol/s)
X	Force(J/mol K or 1/K)
x	Liquid mole fraction (-)
y	Vapor mole fraction (-)
ΔS	Entropy production rate (J/s K)
ℓ	Phenomenologic coefficient (mol^2 K/s J)
λ	Lagrange multiplier (mol/s or J/mol K)
μ	Chemical potential (J/mol)

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