

# Comparison of Entropy Production Rate Minimization Methods for Binary Diabatic Tray Distillation

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## Abstract

The purpose of this study is to compare two analytical methods with two numerical methods for minimizing the entropy production rate in diabatic distillation columns (i.e. with heat exchangers on all trays). The first analytical method is the Equal-Thermodynamic-Distance method. The second uses Lagrange minimization on a model derived from irreversible thermodynamics. The numerical methods use Powell's and a Monte-Carlo algorithm and gave the same results. Both analytical methods agreed well with the numerical ones for two columns with low separation per tray, while they did not agree well for a column with large separation per tray.

*Key words: Diabatic, Distillation, minimum entropy production rate*

## 1. Introduction

This work is inspired by Andresen and Salamon (2000) and De Koeijer and Kjelstrup (2000), in which minimization of entropy production rate of diabatic distillation is discussed. Diabatic distillation columns have heat exchangers on all trays. They are known from Rivero (1993); Le Goff et al. (1996); Agrawal and Fidkowski (1996) to have a better second law efficiency than the normal adiabatic distillation column with only two heat exchangers: the reboiler and the condenser. Besides giving a more prudent use of energy, there are indications that diabatic distillation is also economically feasible, see Tondeur and Kvaalen (1987) and Kauchali et al. (2000). Despite these advantages, diabatic distillation is still relatively unexplored. No design methods are established and there is only one systematic experimental study by Rivero (1993).

The central question is how to obtain maximum second law efficiency or minimum entropy production rate by distributing the heating and cooling capacity over the column, i.e. how to obtain the best duty profile. The design of the column will depend on these results. In recent years four different meth-

ods have been published on how to determine the duty profile. Among these four methods, two are analytical and two are numerical. One analytical method was described by Andresen and Salamon (2000). It is called the principle of Equal Thermodynamic Distance (ETD), and uses the thermodynamic geometry of the system in state space. De Koeijer and Kjelstrup (2000) presented another analytical method together with a numerical method. The analytical method applied Lagrange minimization and irreversible thermodynamics. The numerical method is based on a Monte Carlo algorithm. A second numerical method applies Powell's algorithm (Press et al. (1992)) to a normal entropy balance, see Schaller et al. (2001). All four methods minimize the entropy production rate due to heat and mass transfer on the trays only.

The occurrence of four different methods for one problem created a discussion on the predictive power, accuracy and applicability of those methods. The purpose of this work is to compare these four methods for three example columns. Furthermore, the difference between adiabatic and diabatic columns will be discussed.

We shall see that the numerical methods agree essentially over the whole range of variations. This means that such methods can be used as benchmarks for the analytical methods, and we shall therefore do this. The two analytical methods have different characteristics, and do not always follow the results of the numerical methods. The purpose of analytical methods is to give physical insight.

## 2. The System

The system is a diabatic distillation column, i.e. with heat exchangers on all trays. We use three columns that all separate benzene and toluene. The feed is always  $F=1.00$  mol/s with a feed mole fraction of benzene,  $x_b^F = 0.5$ . TABLE I gives the parameters that differ between the three columns.

TABLE I. COLUMN CHARACTERISTICS

Column	A	B	C
Number of trays	20	20	70
$x_b^B$	0.10	0.01	0.01
$x_b^D$	0.90	0.99	0.99

The most realistic column is column B. Column C has an unreasonable number of trays, while column A has a rather low purity of the products. Physical chemical properties of the binary mixture are given in TABLE II.

TABLE II. PHYSICAL CHEMICAL PROPERTIES

Comp.	Benzene	Toluene
$T^{\text{boil}}(\text{K})$	353.25	383.78
$C_P^{\text{vap}}(\text{J/mol.K})$	81.63	106.01
$C_P^{\text{liq}}(\text{J/mol.K})$	133.50	156.95
$\Delta_{\text{vap}}H(T^{\text{boil}})(\text{J/mol})$	33600	38000
$S_0^{\text{liq}}(\text{J/mol.K})$	269.20	319.74

Tray characteristics are calculated by a top to bottom tray-to-tray calculation with the assumption that equilibrium is established on each tray using Eqs. (1), (2), and (3). Further assumptions are temperature independent heat capacities for both phases and a constant pressure ( $10^5$  Pa). The feed and products are taken to be liquids at their boiling points. The assumption of equimolar overflow is not used, because an incorrect enthalpy balance leads to an incorrect entropy balance. Equilibrium mole fractions for each tray were determined by using an integrated form of the Clausius-Clapeyron equation for a regular solution, see Pitzer and Brewer (1961).

$$y_{b,n} = x_{b,n} \exp \left[ \frac{\omega}{RT_n} (1 - x_{b,n}^2) \right] \exp \left[ \frac{\Delta_{\text{vap}}H_b(T)}{R} \left( \frac{1}{T_b^{\text{boil}}} - \frac{1}{T_n} \right) \right]$$

$$1 - y_{b,n} = (1 - x_{b,n}) \exp \left[ \frac{\omega}{RT_n} x_{b,n}^2 \right] \exp \left[ \frac{\Delta_{\text{vap}}H_t(T)}{R} \left( \frac{1}{T_t^{\text{boil}}} - \frac{1}{T_n} \right) \right] \quad (1)$$

The non-ideality parameter  $\omega$  is 252.50. For each tray number  $n$ , a specified temperature  $T_n$  in Eq. (1) determines the corresponding pair of mole fractions in the gas ( $y_{b,n}$ ) and the liquid ( $x_{b,n}$ ). The mass balances are used to calculate the mass flows ( $L_n$  and  $V_n$ ) on each tray.

$$\begin{aligned} V_n + L_n &= V_{n+1} + L_{n-1} \\ V_n y_{i,n} + L_n x_{i,n} &= V_{n+1} y_{i,n+1} + L_{n-1} x_{i,n-1} \end{aligned} \quad (2)$$

The duties of the heat exchangers are calculated from the energy balance over the tray.

$$V_n H_n^V + L_n H_n^L = V_{n+1} H_{n+1}^V + L_{n-1} H_{n-1}^L + Q_n \quad (3)$$

The entropy production rate on the tray is then given by

$$\left[ \frac{dS^{\text{irr}}}{dt} \right]_n = V_n S_n^V + L_n S_n^L - \frac{Q_n}{T_n} - V_{n+1} S_{n+1}^V - L_{n-1} S_{n-1}^L \quad (4)$$

The feed tray is located on the tray where the liquid mole fraction of benzene becomes lower than the feed mole fraction. From the mass and energy balances on the tray, the total entropy production rate of the whole column is obtained as:

$$\frac{dS^{\text{irr}}}{dt} = BS^B + DS^D - FS^F - \sum_{n=0}^N \frac{Q_n}{T_n} \quad (5)$$

This is the objective function for the equal thermodynamic distance method as well as the two numerical methods.  $Q_0$  is the duty of the heat exchanger that condenses vapor flow  $V_1$  totally, i.e. the condenser.

Alternatively, the objective function can also be set up from knowledge of the transport processes on each tray, using irreversible thermodynamics from Førlund et al. (2001). The entropy production rate of tray  $n$  is

$$\left[ \frac{dS^{\text{irr}}}{dt} \right]_n = J_{q,n} X_{q,n} + J_{b,n} X_{b,n} + J_{t,n} X_{t,n} \quad (6)$$

$J_{q,n}$  is the flow of heat,  $J_{b,n}$  and  $J_{t,n}$  are flows of benzene and toluene across the phase boundary, and  $X_{q,n}$ ,  $X_{b,n}$  and  $X_{t,n}$  are the conjugate driving forces. The objective function is now obtained by summing over all trays. Entropy production in the heat exchangers that supply  $Q_n$  is not included in either of

the objective functions. The adiabatic column is also simulated with the tray-to-tray method where  $Q_2, \dots, Q_{N-1}$  are zero. This means that  $Q_0$  and  $Q_1$  form together the condenser, and  $Q_N$  is the reboiler.

### 3. Powell's method

Powell's algorithm is a multidimensional optimization routine. The entropy production rate, expressed by Eq. (5), is minimized and the corresponding temperature for each tray is determined. Since the temperature  $T_1$  at the top tray and the temperature  $T_N$  at the reboiler are fixed by the given distillate and bottom purity requirements  $x_b^D$  and  $x_b^B$ , the number of control variables is  $M = N - 2$ . As initial guesses  $\tilde{\mathbf{T}}_0$  of temperatures on the trays we used linear temperature profiles in all minimizations. The following procedure was repeated until the entropy production rate stopped decreasing. For each search direction  $\tilde{\mathbf{u}}_j$ ,  $j = 1, \dots, M$  the entropy production rate is minimized along that direction using the temperature profile  $\tilde{\mathbf{T}}_{j-1}$  as starting point. The result of this minimization is saved as  $\tilde{\mathbf{T}}_j$ . The line minimization is performed by a bracketing routine and parabolic interpolation (Brent's method). The direction along which the entropy production made its largest decrease  $\Sigma$  is named  $\tilde{\mathbf{u}}_\Sigma$  and saved as well as the net displacement  $\tilde{\mathbf{T}}_M - \tilde{\mathbf{T}}_0$ . Writing the temperature dependence of the entropy production rate from Eq. (5) as  $\frac{dS^{\text{irr}}}{dt}(\tilde{\mathbf{T}})$ , the following quantities are introduced:

$$\begin{aligned} \xi_0 &\equiv \frac{dS^{\text{irr}}}{dt}(\tilde{\mathbf{T}}_0) & \xi_M &\equiv \frac{dS^{\text{irr}}}{dt}(\tilde{\mathbf{T}}_M) \\ \xi_E &\equiv \frac{dS^{\text{irr}}}{dt}(2\tilde{\mathbf{T}}_M - \tilde{\mathbf{T}}_0) \end{aligned} \quad (7)$$

If at least one of the inequalities

$$\begin{aligned} \xi_E &\geq \xi_0 \quad \text{or} & (8) \\ \frac{2(\xi_0 - 2\xi_M + \xi_E)[(\xi_0 - \xi_M) - \Sigma]}{\Sigma(\xi_0 - \xi_E)^2} &\geq 1, & (9) \end{aligned}$$

holds, then the old search direction set is kept,  $\tilde{\mathbf{T}}_M$  is saved as  $\tilde{\mathbf{T}}_0$ , and the program returns to do another iteration of the algorithm. If both inequalities do not hold, the direction of largest decrease  $\tilde{\mathbf{u}}_\Sigma$  is discarded and  $\tilde{\mathbf{u}}_M$  is assigned to  $\tilde{\mathbf{u}}_\Sigma$ . This avoids a buildup of linear dependence of the search directions.  $(\tilde{\mathbf{T}}_M - \tilde{\mathbf{T}}_0)$  is assigned to  $\tilde{\mathbf{u}}_M$ . A line minimization is done along the new  $\tilde{\mathbf{u}}_M$  and the result is saved as  $\tilde{\mathbf{T}}_0$ . The algorithm is repeated until the required accuracy is achieved.

### 4. Monte Carlo method

The method was in essence presented by De Koeijer and Kjelstrup (2000). The Monte

Carlo algorithm starts from either a linear temperature profile or a temperature profile of the adiabatic column. It changes on a random tray the temperature with a random step that is multiplied with a factor  $f$ . If the entropy production rate of the new profile is larger, or if the profile is not physically realizable, the profile is rejected, and a new random step is tried on the previous profile. If the entropy production rate is lower, the new profile is accepted as a new starting point for a new random step on a random tray. This procedure is repeated 2000 times. Then the factor  $f$  is decreased, and the procedure is repeated again. The factor  $f$  decreases exponentially in 7 steps. When the factor  $f$  reaches its lowest value, the resulting minimum is recorded. In order to test whether this minimum can be lowered, the temperature on one random tray is changed, i.e the temperature profile is perturbed. The whole procedure is repeated again up to 1000 times. If there is no change in the course of one day, the procedure is stopped and a minimum is obtained.

### 5. Equal Thermodynamic Distance

Thermodynamic distance measures the length of a path in the set of equilibrium states of a thermodynamic system. The system of relevance for the present discussion is a two phase binary mixture. An equilibrium state of this mixture is specified once we are given the temperature and the number of moles of liquid and vapor. The path of interest is defined using the temperature  $T$  as the parameter, where  $L(T)$  and  $V(T)$  are obtained by solving the mass balance conditions corresponding to the limit of an infinite number of trays to give

$$V(T) = \frac{x_D - x(T)}{y(T) - x(T)}D \quad (10)$$

$$L(T) = \frac{x_D - y(T)}{y(T) - x(T)}D, \quad (11)$$

above the feed and

$$V(T) = \frac{x(T) - x_B}{y(T) - x(T)}B \quad (12)$$

$$L(T) = \frac{y(T) - x_B}{y(T) - x(T)}B \quad (13)$$

below the feed. The discontinuity at the feed is handled by an isothermal path along which the quantities  $L$  and  $V$  change linearly. It makes no difference how we move across this portion of the path. As long as we keep the temperature constant, this portion of the path is associated with zero length and zero dissipation, see Salamon and Nulton (1998).

According to the principle of equal thermodynamic distance (ETD, Nulton et al. (1985); Salamon and Nulton (1998); Andresen and Salamon (2000)), the optimal way to traverse this path using a sequence of  $N$  equilibrations is in equidistant stages, i.e. such that the distance along that path between the  $n$ -th and the  $n+1$ -th tray be the same for all  $n$ . In general, distance is measured by using the second derivative of the entropy of the system with respect to the extensive variables as a Riemannian metric (Ruppeiner (1995)). In this particular case, this reduces to a simpler expression, with the infinitesimal length  $d\mathcal{L}$  being given by

$$d\mathcal{L} = \sqrt{\sum_{i,j} \frac{\partial^2 S}{\partial Z_i \partial Z_j} dZ_i dZ_j} = \frac{\sqrt{C_\sigma}}{T} dT, \quad (14)$$

where the  $Z_i$  are the extensive variables of the system and  $C_\sigma$  is the constant pressure coexistence heat capacity (Salamon and Nulton (1998); Andresen and Salamon (2000)), i.e. the heat capacity that a sample consisting of  $L(T)$  moles of liquid and  $V(T)$  moles of vapor has while the two phases coexist at constant pressure. In order to establish an ETD path from the condenser  $T_0$  to the reboiler  $T_N$  in a column with  $N$  trays, one has to determine temperatures  $T_n$  such that

$$\int_{T_n}^{T_{n+1}} \frac{\sqrt{C_\sigma}}{T} dT = \frac{1}{N} \int_{T_0}^{T_N} \frac{\sqrt{C_\sigma}}{T} dT, \quad n = 0, \dots, N-1. \quad (15)$$

The equal thermodynamic distance principle is derived by approximating the entropy production rate to lowest nonzero order in  $1/N$ . For a small equilibration, the entropy production rate is quadratic to lowest order and this quadratic part is (by definition) the square of the length element. Minimizing the sum of the squares of the lengths with the constraint of constant total length yields the equal thermodynamic distance principle. The sequence of temperatures obtained is then used as the temperature profile for the calculation of column parameters as described in the previous section. Note that the mass flow rates  $L_n$  and  $V_n$  obtained in this fashion do not lie on the curve  $L(T)$ ,  $V(T)$  used for the determination of the temperature profile, although they do fall close to the curve and approach it as  $N \rightarrow \infty$ . The entropy production rate obtained by this procedure turns out to match the optimal entropy production to third order in  $1/N$ , see Nulton and Salamon (2001).

A known limitation of the ETD-method is the requirement for a minimum column length. This limitation is due to the fact that

the tray-tray separation cannot get too large. In particular,

$$x_{n-1} \leq y_n \quad (16)$$

is a fundamental physical constraint on how far apart two adjacent trays in a distillation column can be. For a certain total length  $\mathcal{L}$  and number of trays  $N$ , each ETD step must go a distance  $\mathcal{L}/N$ . For  $N$  sufficiently large, condition (16) is never a problem. The condition typically becomes a problem already for column lengths about 50% longer than conventional.

## 6. Lagrange minimization with irreversible thermodynamics

The three fluxes and forces of heat and mass transport that are given in Eq. (6) cannot be used without knowledge of the transport processes. In distillation these transport processes vary across the phase boundary of one tray  $n$ , and some average and integration procedures are needed. When one uses the assumption of equilibrium between gas and liquid at the outlet of a tray, integrated fluxes and average forces can be defined, see De Koeijer and Kjelstrup (2000) and De Koeijer et al. (1999). It is also assumed that the entropy production rate stems from the gas side of the phase boundary, and that there is a negligible contribution from the thermal force, see also Kjelstrup-Ratkje et al. (1995). The driving forces are then related via the Gibbs-Duhem equation. The entropy production rate of a column is:

$$\begin{aligned} \sum_{n=1}^N \left[ \frac{dS_{\text{irr}}}{dt} \right]_n &= \sum_{n=1}^N (J_{b,n} X_{b,n} + J_{t,n} X_{t,n}) \\ &= \sum_{n=1}^N (J_{b,n} - \bar{y}_n J_{t,n}) X_{b,n} \end{aligned} \quad (17)$$

where  $J_{b,n}$  and  $J_{t,n}$  are flows of benzene and toluene across the phase boundary in mol/s, and  $X_{b,n}$  and  $X_{t,n}$  are the corresponding driving forces, and  $\bar{y}_n$  is the average mole fraction ratio in the Gibbs-Duhem equation. On tray number  $n$ , the average driving force for benzene is:

$$X_{b,n} = R \ln \left( \frac{y_{b,n}}{y_{b,n+1}} \right). \quad (18)$$

De Koeijer and Kjelstrup (2000) showed that this model was a good approximation to Eq. (4) for two columns. The sum of the contributions from all trays is minimized with the Lagrange method as follows:

$$\begin{aligned} \text{minimize} \quad & \sum_{n=1}^N \left[ \frac{dS_{\text{irr}}}{dt} \right]_n = \\ & \sum_{n=1}^N (\ell_{bn} - \bar{y}_n \ell_{tn}) X_{b,n}^2 \end{aligned} \quad (19)$$

subject to:

$$\begin{aligned} R \ln \left( \frac{x_b^D}{x_b} \right) &= \sum_{n=1}^N X_{b,n} = I_1 \\ R \ln \left( \frac{x_t^D}{x_t} \right) &= \sum_{n=1}^N X_{t,n} = I_2 \\ Fx_b^F - Bx_b^B &= \sum_{n=1}^N J_{b,n} = I_3 \\ Fx_t^F - Bx_t^B &= \sum_{n=1}^N J_{t,n} = I_4 \end{aligned} \quad (20)$$

The four constraints in Eq. (20) ensure that the production level and the purity of products are as required. The solution has the following structure:

$$\begin{bmatrix} 1 & 1 & \cdot & 1 \\ -\bar{y}_1 & -\bar{y}_2 & \cdot & -\bar{y}_N \\ \ell_{b,1} & \ell_{b,2} & \cdot & \ell_{b,N} \\ \ell_{t,1} & \ell_{t,2} & \cdot & \ell_{t,N} \end{bmatrix} \begin{bmatrix} X_{b,1} \\ X_{b,2} \\ \cdot \\ X_{b,N} \end{bmatrix} = \begin{bmatrix} I_1 \\ I_2 \\ I_3 \\ I_4 \end{bmatrix} \quad (21)$$

$$\begin{bmatrix} -\ell_{b,1} & -\ell_{t,1} & -1 & \bar{y}_1 \\ -\ell_{b,2} & -\ell_{t,2} & -1 & \bar{y}_2 \\ \cdot & \cdot & \cdot & \cdot \\ -\ell_{b,N} & -\ell_{t,N} & -1 & \bar{y}_N \end{bmatrix} \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ \lambda_3 \\ \lambda_4 \end{bmatrix} = \begin{bmatrix} 2(\ell_{b,1} - \bar{y}_1 \ell_{t,1}) X_{b,1} \\ 2(\ell_{b,2} - \bar{y}_2 \ell_{t,2}) X_{b,2} \\ \cdot \\ 2(\ell_{b,N} - \bar{y}_N \ell_{t,N}) X_{b,N} \end{bmatrix} \quad (22)$$

Eq. (21) is a rewriting of the constraints while Eq. (22) is the actual solution of the Lagrange minimization. Together they should form a solvable set of equations and unknowns. A solution will be consistent with the assumption of equilibrium on the outlet of all trays, but has not been found yet. In order to check how the theory performs, we use linear regression on Eq. (22). The resulting correlation coefficient and standard errors give an indication

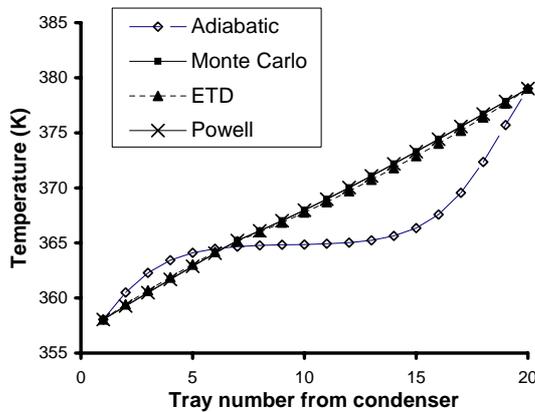


Figure 1. Temperature profiles of column A

how accurate results of this method can be.

## 7. Results and discussion

### 7.1. Minimization results

The minimum entropy production rate of the columns are calculated from Eq. (5) (including the contribution of the feed and products), after the ETD, Powell's and Monte Carlo minimizations are done. The results are given in TABLE III. The entropy production rates of the corresponding adiabatic columns are included for comparison, see discussion further on in this section.

TABLE III. TOTAL ENTROPY PRODUCTION IN W/K OF THE ADIABATIC AND DIABATIC COLUMNS

	Adia- batic	ETD	Powell	Monte Carlo
A	2.1687	0.78211	0.77723	0.77692
B	4.0357	(1.4887)	3.3007	3.2977
C	3.0724	0.61202	0.60508	0.60136

In all cases, the Monte Carlo method gave the lowest entropy production rates, followed closely by Powell's method. The ETD method gave a lower value for column B, but this result was not physically realizable because it had a negative vapor and liquid flow in the top and bottom of the column. For all columns the reduction in entropy production rate compared to the adiabatic operation was significant. Figures 1, 3 and 5 show the temperature profiles resulting from the ETD, Monte Carlo, and the Powell's minimization methods. The temperature profiles of the adiabatic simulation are included for comparison. The corresponding duty profiles of all columns are presented in figures 2, 4 and 6, which are the answer to the central question posed in the introduction.

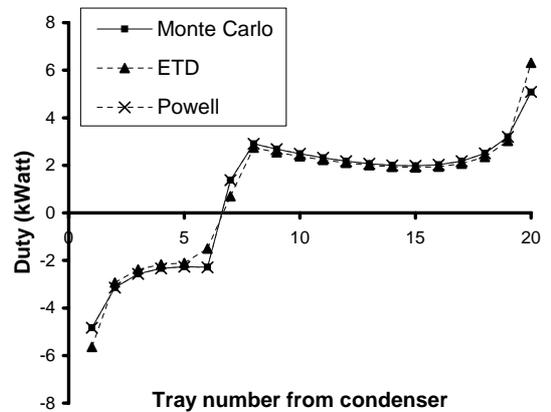


Figure 2. Duty profiles of column A

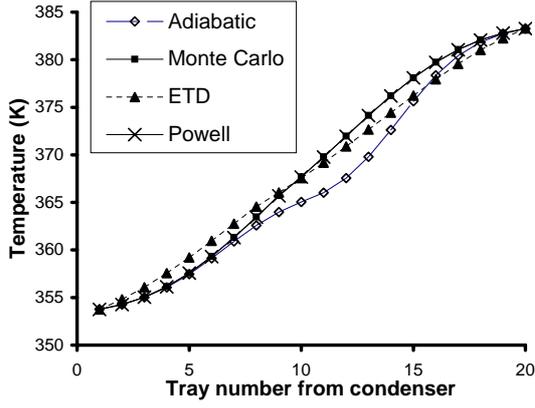


Figure 3. Temperature profiles of column B

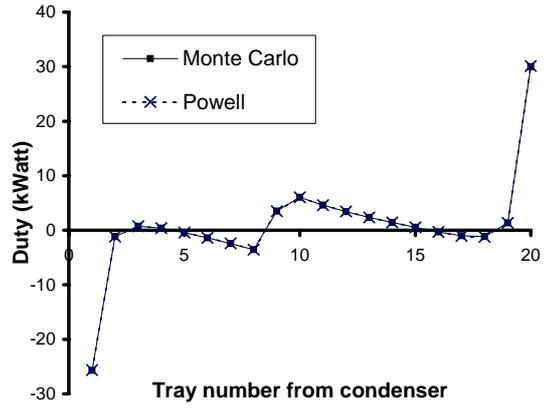


Figure 4. Duty profiles of column B

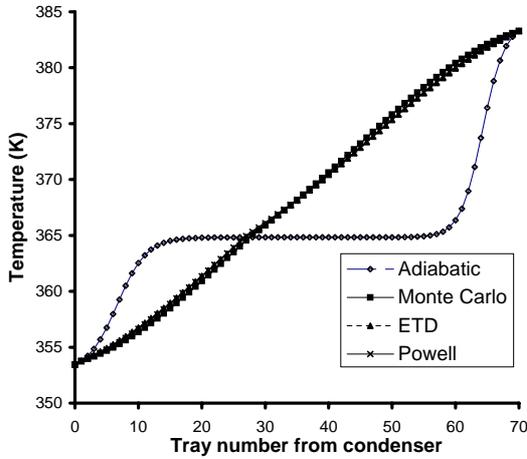


Figure 5. Temperature profiles of column C

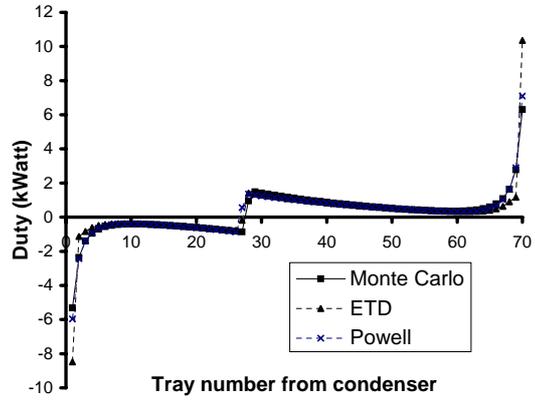


Figure 6. Duty profiles of column C

The results of the three minimization methods are nearly indistinguishable for column A, but not for columns B and C. Furthermore, the profiles of the adiabatic columns differ a lot from those of the columns with minimum entropy production. This will be discussed later.

TABLE IV presents the results of the application of the Lagrange minimization on irreversible thermodynamics. It consists of the values of the Lagrange multipliers and their standard errors and the total correlation coefficients. All values were calculated using linear regression of Eq. (22) on the data from the

Monte Carlo method. The correlation coefficient and standard errors were best for column A, thereafter C and finally B.

## 7.2. Comparison of the methods

We start with the methods giving the best results: the numerical ones. TABLE III and figures 1, 2, 3, 4, 5, and 6 give confidence to both numerical methods because their results essentially agree for all three columns. The results that the total entropy production rate increases by decreasing the number of trays from 70 (C) to 20 (B), or by increasing the purity of the production from 10 % (A) to 1% (B), are as expected.

TABLE IV. LAGRANGE MULTIPLIERS OF THE MINIMUM ENTROPY PRODUCING COLUMNS CALCULATED WITH LINEAR REGRESSION

referring to		A	B	C	Unit
$\lambda_1$	$\ell_1$	$-0.213 \pm 0.018$	$-0.167 \pm 0.021$	$0.0775 \pm 0.0055$	J/mol K
$\lambda_2$	$\ell_2$	$0.917 \pm 0.051$	$3.65 \pm 0.48$	$-0.712 \pm 0.035$	J/mol K
$\lambda_3$	intercept	$-0.0462 \pm 0.0039$	$-0.123 \pm 0.033$	$0.0276 \pm 0.0022$	mol/s
$\lambda_4$	$\bar{y}_n$	$0.0277 \pm 0.0018$	$0.0256 \pm 0.0033$	$-0.00721 \pm 0.00026$	mol/s
$R^2$		0.995	0.966	0.983	

The lower entropy production rate of adiabatic column, compared to that of an adiabatic column, gives the rationale for all minimization methods. We know that neither method guarantees a global minimum. But the near equality of the results gives us confidence that we have actually obtained the global minimum with both numerical methods. The Monte Carlo algorithm resulted in a slightly lower entropy production rate than Powell’s algorithm, see TABLE III. This is presumably due to inaccuracies in the estimated gradient obtained by Powell’s method. However, the Monte Carlo algorithm took more time to get to the minimum than Powell’s algorithm did. The Monte Carlo method gave a steady minimum after several hours, sometimes days, while Powell’s method was ready after 1-2 hours. In general, for Powell’s method, minimum entropy production was obtained after a few N iterations using a relative accuracy of  $10^{-9}$ . In judging the results, it should also be kept in mind that different computers were used. However, the difference in time is reasonable because the Monte Carlo algorithm used most of the computing effort on calculations of temperature profiles that were nonphysical, or that had a higher entropy production rate. We conclude that the results of both numerical methods can be taken as a benchmark for the evaluation of analytical methods.

A singularity problem may arise using Powell’s algorithm. The entropy production in Eq. (5) consists of terms of the form  $Q_n/T_n$  which in turn are functions of the liquid and vapor flows  $V_n$  and  $L_n$ . An explicit representation of the vapor flow above the feed is given by

$$V_n(T_n, T_{n-1}) = \frac{x_b^D - x_{b,n-1}(T_{n-1})}{y_{b,n}(T_n) - x_{b,n-1}(T_{n-1})} D \quad (23)$$

Analogous expressions exist for the liquid flows and the trays below the feed. Eq. 23 has a singularity; the flow becomes infinite for  $y_{b,n} = x_{b,n-1}$ . This leads to an undesired instability of the minimization algorithm: At the beginning of a line minimization along a particular search direction the minimum needs to be bracketed. Otherwise, the one-dimensional minimization routine may jump over this singularity and lead to a nonphysical result, e.g. a large negative value for the entropy production.

The method of equal thermodynamic distance (ETD) permits a direct comparison with the numerical methods from the data in TABLE III and *Figures 1, 2, 3, 4, 5, and 6*. It is observed that ETD predicted column A better

than columns B and C. The maximum deviations with the Monte Carlo benchmark results in predicted temperatures were 0.40 K on tray 15 in column A, 1.87 K on tray 15 in column B and 0.53 K on tray 56 in column C. The duty profile of ETD is not given for column B in *figure 4* because the solution was nonphysical. Specifically, it had extremely high duties with opposite signs at both ends of the column. As a consequence it gave (impossible) negative liquid flows on tray 1 (-2.3 mol/s) and 19 (-1.46 mol/s) and negative vapor flows on tray 2 (-1.84 mol/s) and 20 (-1.96 mol/s). This is due to the already mentioned limitation of the ETD method that the tray-tray separation stay small as discussed in connection with Eq. 16. Column B does not have enough trays for the required thermodynamic distance. For columns of length comparable to what would currently be used in an industrial implementation (like column B), condition (16) is invariably violated. This is why column A and C, but not B is well predicted by this method. Concluding, ETD gives good results for columns with large number of trays and/or low purities of which the assumption of equilibrium on each tray is valid. But once a low number of trays and/or high purity products or non-equilibrium modeling are demanded it loses its reliability.

Both objective functions, the entropy balance in Eq. (5) and Eq. (17) from irreversible thermodynamics, describe in principle the same column. Their approaches and assumptions differ, however. We have chosen previously the results of the numerical methods that use Eq. (5) as a benchmark. The correlation coefficients and standard errors from TABLE IV give therefore an indication how accurate the method, using Lagrange minimization on Eq. (17) with the constraints in Eq. (20), describes the benchmark results. De Koeijer and Kjelstrup (2000) give arguments and results for the correctness of the Lagrange minimization with the constraints in Eq. (20). So, the correlation coefficients and standard errors become a measure of the accuracy of Eq. (17). The near unity correlation coefficient for column A can be interpreted by Eq. (17) being an accurate approximation of Eq. (5). The correlation coefficient for column B is 0.966. This means that Eq. (17) is a poorer approximation of Eq. (5) for column B than for A. Inaccurate (and possibly nonphysical) solutions may show up for column B by solving Eqs. (21) and (22). The results for column C are better than for B, but not as good as for column A. Out of the three columns here and two earlier ones in De Koeijer and Kjelstrup (2000), four columns have had correlation coefficients better than 0.98 for this

method. The lower correlation coefficients are observed for the columns with high purities and/or hard separation. So, we can say that the assumptions behind Eq. (17) are not valid for columns operating with these conditions.

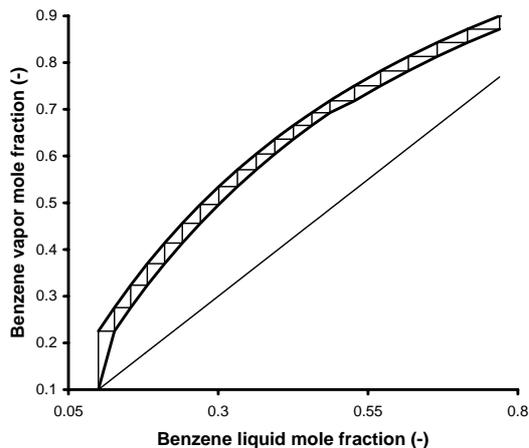
The Lagrange minimization with irreversible thermodynamics does not provide (yet) an actual solution, but it has a potential for further development. It gives a systematic way of modeling non-equilibrium phenomena, and does not necessarily depend on the assumption of equilibrium on the outlet of all trays. Wesselingh (1997) argues even that this equilibrium assumption leads to results that have no connection to real distillation columns. In this perspective, these results can be considered as a base for further work.

There are several differences between the two analytical methods. The first method, ETD, is based on a lowest order asymptotic analysis of the path over the equilibrium surface. The second method with the Lagrange minimization uses irreversible thermodynamics. The objective function, the entropy production rate, is expressed differently. The ETD method uses the total entropy balance of the system. Irreversible thermodynamics uses the sum of flux-force products of the processes that take place. But their differences have not really been tested here, because the assumption of equilibrium on each tray has been used to find both objective functions. The accuracy of the methods is dependent on what type of information is needed. The ETD method uses information about equilibrium states, while the second method requires a model of the (non-equilibrium) processes in

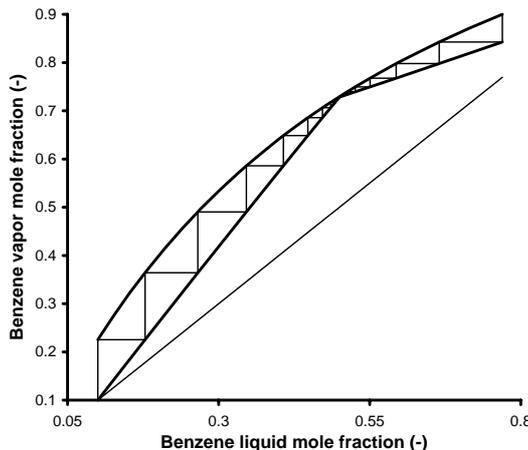
terms of fluxes, forces and phenomenologic coefficients. The ETD method can then only be accurate if the column operates close to equilibrium and if it has a relatively high number of trays. It has not been tested yet how far from equilibrium the ETD method still predicts accurately. The accuracy of the second method depends on how good that particular model describes reality. Relating these differences to the present work, the ETD method does not describe column B accurately due to the relatively low number of trays, while Lagrange minimization and irreversible thermodynamics fails for column B due to an inaccurate model.

### 7.3. Diabatic versus adiabatic columns

Finally we discuss in more depth the common purpose of the minimization methods: minimizing entropy production rate by adding heat exchangers on each tray. The McCabe-Thiele diagram of diabatic operation with minimum entropy production is given for column A in *figure 7*. *Figure 8* shows the McCabe-Thiele diagram of the corresponding adiabatic column A. The operating line is more parallel to the equilibrium line in a diabatic column than in an adiabatic column. This behavior was observed for a rectifying column in Sauar et al. (1997), but not before for a total column. Sauar et al. (1997) found this to be consistent with equipartition of forces for larger parts of the column. The diagram in *figure 8* indicates already that there is room for improvement in the adiabatic column, as the trays around the feed do not perform a reasonable separation, i.e. this adiabatic column is badly designed from a second law perspective.



*Figure 7. McCabe-Thiele diagram of diabatic column A with minimum entropy production rate*



*Figure 8. McCabe-Thiele diagram of adiabatic column A*

In order to illustrate the difference between adiabatic and diabatic columns further, we give the vapor and liquid flow profiles of column A in *figures 9* and *10*. The discontinuity in the liquid profiles is due to the feed, which is a liquid at its boiling point. This location of the feed tray is moved from tray 9 in the adiabatic to tray 7 in the diabatic column, i.e the stripping section is enlarged. We see that the vapor flow is rather constant for the adiabatic column. This allows the normal column design with constant diameter because the diameter is roughly proportional to the vapor flow. The vapor flow in a diabatic column is not constant. Design of a column that allows this behavior of the vapor flow, is clearly a challenge for chemical engineers. A constant diameter may increase the risk for uneven pressure drops, flooding or dry-up. On the other side, a column with a varying diameter is more expensive.

Neither the entropy production rate (Tondeur and Kvaalen (1987)) nor the driving force for mass transport (Saurar et al. (1996)) are constant in the diabatic column A with minimum entropy production rate. *Figures 11* and *12* show the benzene driving force from Eq. (18) and the entropy production rate from Eq. (17) as a function of the tray number counted from the condenser. The entropy production varies by a factor of two over the diabatic column. The force varies even more. A constant force through the column is also not expected, given the nature of the constraints in Eq. (20), see Bedeaux et al. (1999). *Figures 11* and *12* do show, however, that separation work is moved from the top and bottom ends to the middle part as a consequence of the minimization, and that the variation in the force as well as in the entropy production rate is more uniform in the diabatic than in the adiabatic column.

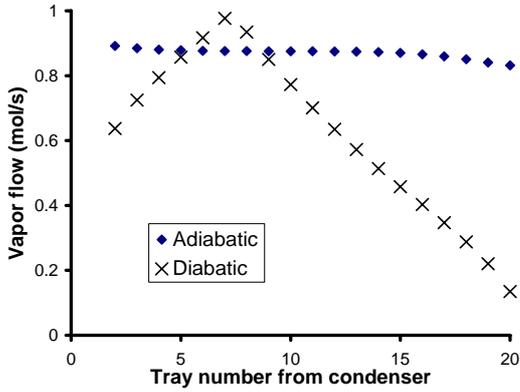


Figure 9. Vapor flow profile of column A

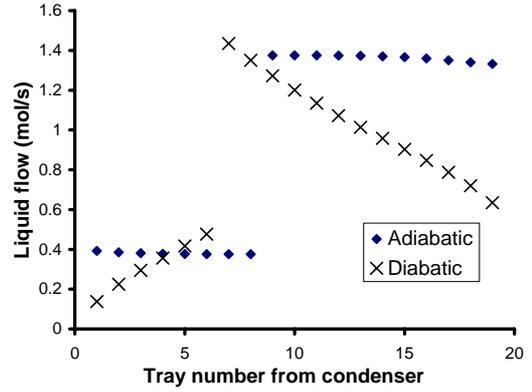


Figure 10. Liquid profile of column A

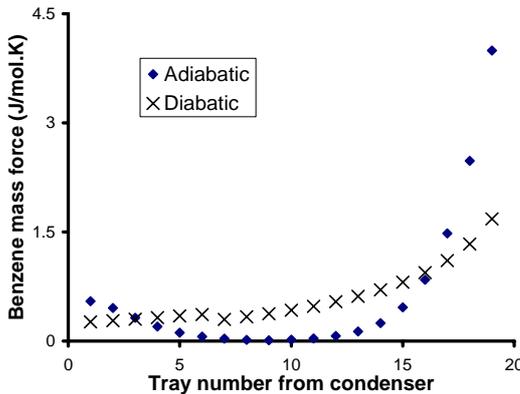


Figure 11. Benzene mass force profile of adiabatic and diabatic column A

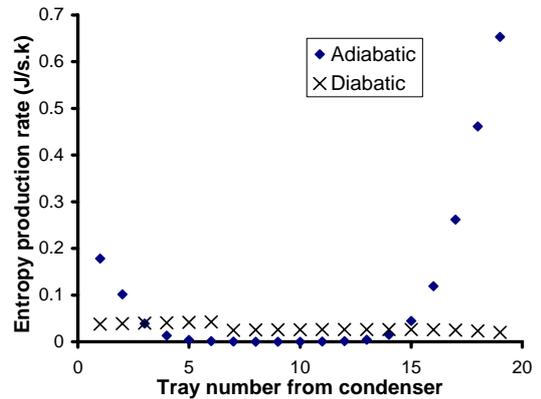


Figure 12. Entropy production rate calculated with Eq. (17) of adiabatic and diabatic column A

## 8. Conclusions

Two analytical and two numerical methods for minimizing entropy production rate in diabatic binary distillation are compared. The two numerical methods, which are based on Powell's method and a Monte Carlo algorithm, give similar results and the lowest entropy production rates. The analytical method of Equal Thermodynamic Distance (ETD) gives results that are in agreement with the numerical methods for two columns with a large number of trays and/or low purity products. However, for a column with high purity products and low number of trays, it gives a nonphysical solution. The analytical method based on applying Lagrange minimization on irreversible thermodynamics gives no direct result but its solution is in agreement with the numerically obtained minima for the same two columns as ETD, according to a linear regression analysis. Lagrange minimization also describes inaccurately the results for column B, the same column for which ETD gives a nonphysical solution. More work is clearly needed to make the analytical methods useful. In the meantime, the numerical methods may serve the practical purpose of optimization.

Only the entropy production rate due to tray processes are taken into account in the above calculations. The contribution to the entropy production rate from the heat exchangers is not considered. Such contributions will change the relative gain from making the column diabatic.

Even though the analytical methods presented still have their limitations, it is important to note that there are now highly effective numerical methods available for the design and analysis of diabatic distillation columns. The second law gains available from such columns world wide are very significant, especially in an environment where the CO<sub>2</sub> production should be reduced to levels well below current values. We believe that the methods presented here, especially the analytical ones, offer ample opportunities for further research in this field.

### Acknowledgments

The Telluride Research Center is thanked for hosting the workshop at which this cooperation was initiated. The Research Council of Norway is thanked for a grant to Gelein de Koeijer.

### Symbols

B	Bottom (mol/s)
C <sub>σ</sub>	Constant pressure coexistence heat capacity(J/K)

D	Distillate (mol/s)
F	Feed (mol/s)
H	Enthalpy (J/mol)
I	Value of constraint(mol/s or J/mol K)
J	Flow through phase boundary(mol/s or J/s)
L	Liquid flow(mol/s)
d $\mathcal{L}$	Thermodynamic length( $\sqrt{J/K}$ )
$\ell$	Phenomenologic coefficient (mol <sup>2</sup> K/s J)
M	Number of search directions in Powell's algorithm (-)
N	Number of Trays (-)
Q	Duty(J/s)
R	Gas constant (J/mol K)
R <sup>2</sup>	Correlation coefficient(-)
S	Entropy (J/mol K)
T	Temperature (K)
Z	Extensive variables of the system(various)
$\tilde{T}$	Temperature profile (K)
$\tilde{u}$	Search direction (K)
V	Vapor flow(mol/s)
X	Force(J/mol K or 1/K)
x	Liquid mole fraction (-)
y	Vapor mole fraction (-)
$\bar{y}$	Averaged Gibbs-Duhem vapor mole fraction ratio, see De Koeijer and Kjelstrup (2000)(-)
$\frac{dS^{irr}}{dt}$	Entropy production rate (J/s K)
$\lambda$	Lagrange multiplier (mol/s or J/mol K )
$\Sigma$	Largest decrease in Powell's algorithm (J/s K)
$\xi$	Definition introduced in Eq. 7
$\omega$	Non-ideality parameter(-)

### List of super- and subscripts

B	Bottom
b	Benzene
boil	Boiling
D	Distillate
E	Extrapolated point in Eq. 7
i	Component number i
j	Search direction index in Powell's algorithm
L	Liquid
n	Tray number n
N	Total number of trays
t	Toluene
V	Vapor

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