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Entropy Flow and Energy Efficiency Analysis of Extractive Distillation with a Heavy Entrainer

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ABSTRACT: The minimization of the entropy production is equivalent to minimizing the work or energy consumption required by a separation process. Sources of entropy creation during the extractive distillation of a minimum- and maximum-boiling azeotropic mixture with a heavy entrainer are evaluated at each column stage in accordance with the second law of thermodynamics, and the distribution of entropy flow in different sections of the column is analyzed. Results show that mixing on feed trays and heat exchange in the reboiler and condenser are the main sources of entropy production. The temperature of the main feed and entrainer feed does not significantly affect the irreversibility of the process at the reference temperature of all flows. Although optimal values can be proposed to achieve a minimum isothermal work, the energy loss of the real process steadily increases with increases in the entrainer/feed flow rate ratio and reflux. The influence of the feed tray shows that product purity tends to vary inversely with energy loss.

1. INTRODUCTION

Distillation is a widely used separation technique that requires significant input of energy. The thermodynamic efficiency of the distillation process is often expressed in terms of total energy consumption. Alternatively, the second law of thermodynamics shows where energy losses occur and where modifications could be made to increase the overall utilization of energy in the column and improve performance.[1]

A common way of reducing dissipated energy is to increase the process reversibility. The irreversibility in a distillation column comes from the driving forces that make the separation possible. Distillation can be regarded as a reversible process when it is performed at minimum driving force and equilibrium state.[2] Reducing the irreversibility of distillation processes has received extensive attention. For example, Nakaiwa et al.[3] conducted a parameter analysis and optimization of the internally heat-integrated distillation column (HIDiC), an energy efficient column. Rivero[4,5] studied the optimization of adiabatic and diabatic binary distillation, where heat is added to or withdrawn from each tray by heat exchangers.

Extractive distillation is defined as distillation in the presence of an entrainer fed at a location different from that of the main feed. The entrainer is added to the azeotropic mixture to alter the relative volatility of the key component without additional azeotrope formation, and for many years only heavy boiling entrainers were considered.[6,7] Generally, the entrainer is fed in the upper part of the column, above the feed stream, and it remains at a high concentration in the liquid phase in stages below its introduction into the column.

Reversible distillation columns have second law efficiencies better than those of irreversible distillation columns.[8] The first and the second laws may be used simultaneously to determine the departure from the reversible limitation in terms of the entropy generation of the system. Indeed, entropy is an alternative for energy optimization. Once the minimum entropy generation design is determined for the system, it provides a target for other, more realistic, designs.[9,10]

It is well-known that mixing processes occur spontaneously in nature and they are highly irreversible; the reverse process of spontaneous mixture separation into its pure components is impossible. During a mixing process, some recoverable work is lost. In contrast, during a separation process, the potential work must be replenished. The lost work is proportional to the entropy generation. The entropy production approach leads to showing the location of energy losses as well as their causes,[11−13] and it serves to explain the effect of operational conditions and equipment design on energy efficiency; meanwhile, the entropy production approach helps to define the optimum conditions for minimizing the energy losses.[14,15]

New process opportunities have arisen since the publication of new insights into the design and synthesis of feasible extractive distillation processes with a heavy entrainer.[16,17] Shen et al.[18,19] proposed an extension of thermodynamic insights derived from batch extractive distillation to continuous operation for azeotropic mixtures with a heavy or light entrainer. However, in those processes, many questions remain to be answered, such as how does the reflux ratio, the entrainer/feed flow rate ratio, and the temperature of the main feed and entrainer feed affect the entropy production and thus process efficiency. In the present work, we focus on the sensitivity analysis of the aforementioned operating parameters on the entropy generation and on the
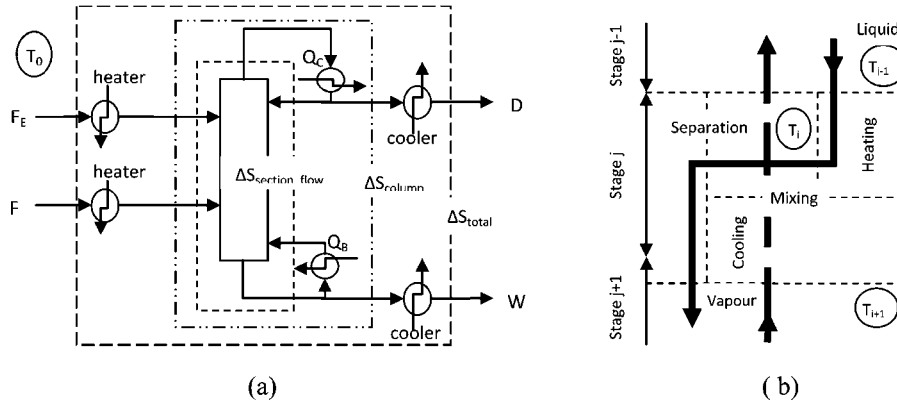
Figure 1. (a) Configuration of extractive distillation column; (b) schematic diagram of equilibrium stage in an adiabatic column.

energy efficiency of the extractive distillation column with a heavy entrainer. The entrainer recovery column is not considered here.

2. CALCULATION AND ASSESSMENT APPROACH

2.1. Calculation of Entropy Production. Unlike azeotropic distillation, in which the entrainer is added along with the main feed, the entrainer is fed to a tray above the main feed in extractive distillation, as shown in Figure 1a. We assume that the distillation process takes place under adiabatic conditions through the exchange of mass and heat between the downward flowing liquid and the upward flowing vapor. All of the heat is supplied by the reboiler Q_B and provided at temperature T_B, which corresponds to the maximum temperature of the distillation process. The cooling Q_C is provided at T_C, which is the minimum temperature.

The entropy balance is used to quantify the total entropy production in a column section as well as in the reboiler and condenser. Figure 1b shows mixing takes place at the jth stage of the column and temperature T_j. The liquid stream L_{j-1} descending from the $(j-1)$th stage must be preheated to T_j, and similarly the vapor stream V_{j+1} in state a rising from the $(j+1)$th stage must be precooled to T_j. Stages are numbered from the top down.

The steady-state entropy balance for a separation process is a summation of the physical contribution due to energy exchange and the chemical contribution related to inflows and outflows. The entropy flows are calculated from eqs 1 and 2:

$$S_j^L = L_j\left(\sum x_{ij}\left(S_i^{0L} + C_{pi}^L \ln\frac{T_j}{T_0}\right) - R\sum x_{ij}\ln\gamma_{ij}x_{ij}\right) \quad (1)$$

$$S_j^V = V_j\left(\sum y_{ij}\left(S_i^{0V} + C_{Pi}^V \ln\frac{T_j}{T_0} + R\ln\frac{P_i^0}{P_T}\right)\right.$$
$$\left. - R\sum y_{ij}\ln y_{ij}\frac{P_T}{P_i^0}\right) \quad (2)$$

Each stage of the distillation column is represented by the combination of two processes: the mixing of liquid and vapor flows (L_{j-1} and V_{j+1}) and the separation into two liquid and vapor streams at equilibrium (V_j and L_j). The flow mixing entropy S_{mix} and the flow separation entropy S_{sep} are given by eqs 3 and 4, respectively:

$$S_{in,j} = S_{mix,j} = S_{j-1}^L + S_{j+1}^V \quad (3)$$

$$S_{out,j} = S_{sep,j} = S_j^L + S_j^V \quad (4)$$

The entropy production on jth stage comes from the difference between the entropy flows into and out of this stage and is given by by eq 5:

$$\Delta S_j = S_{out,j} - S_{in,j} \quad (5)$$

The entropy production in a column section without reboiler and condenser $\Delta S_{section\_flow}$ is given by

$$\Delta S_{section\_flow} = \sum_j S_{out,j} - \sum_{jj} S_{in,j} = \sum_j S_{sep,j} - \sum_j S_{mix,j} \quad (6)$$

The entropy production of the entire extractive distillation column is obtained from

$$\Delta S_{column} = \Delta S_C + \Delta S_B + \Delta S_{section.flow} - S_F - S_{FE} \quad (7)$$

with the entropy production in the condenser

$$\Delta S_C = V_1(S_C^L - S_1^V) + \frac{Q_C}{T_C} \quad (8)$$

and the entropy production in the reboiler

$$\Delta S_B = V_B S_B^V + W S_B^L - L_n S_n^L - \frac{Q_B}{T_B} \quad (9)$$

The overall entropy production of the extractive distillation process combined with the entropy production related to the heating and cooling of the inflows and outflows with respect to the ambient temperature are found from

$$\Delta S_{total} = \Delta S_{column} + \sum \Delta S_{coolers} + \sum \Delta S_{heaters} \quad (10)$$

where the entropy production contributed by the heater is

$$\Delta S_{heater} = (S_{flow,out} - S_{flow,in})_{heater} - \left(\frac{Q_{heater}}{T_{heater}}\right) \quad (11)$$

and the entropy production contributed by the cooler is

$$\Delta S_{cooler} = (S_{flow,out} - S_{flow,in})_{cooler} + \left(\frac{Q_{cooler}}{T_{cooler}}\right) \quad (12)$$

A useful measure for the process inefficiency can be evaluated by the irreversibility process using the well-known Gouy–Stodola relation:[20]

$$LW = T_0\Delta S_{total} \quad \text{where } \Delta S_{total} \geq 0 \quad (13)$$

$$I_{\text{total}} = T_0 \Delta S_{\text{total}} \tag{14}$$

$$I_{\text{column}} = T_0 \Delta S_{\text{column}} \tag{15}$$

The lost work LW is always positive, and it is proportional to the energy inefficiency.

In accordance with the first law of thermodynamics, the steady-state energy balance for the distillation column can be written as

$$Q_B - Q_C = H_D + H_W - H_F - H_{FE} \tag{16}$$

The isothermal minimum reversible molar work of separation at $T_0 = 298.15$ K for a nonideal mixture is given by[20]

$$W_{\min, T_0} = RT_0 [F \sum_i (x_{iF} \ln \gamma_{iF} x_{iF}) + F_E(x_E \ln \gamma_E x_E) - D$$
$$\sum_i x_{iD} \ln \gamma_{iD} x_{iD} - W \sum_i x_{iW} \ln \gamma_{iW} x_{iW}] \tag{17}$$

The second law efficiency measures the fraction of the part of total exergy input which is not lost by the irreversible processes:

$$\eta = \frac{W_{\min}}{W_{\min} + \text{LW}} \tag{18}$$

For an energy-demanding process, the rational efficiency in accordance with the second law of thermodynamics can be defined according to Gomez-Munos et al.[21] and De Nevers et al.:[22]

$$\Delta S_B \% = (\Delta S_B / \Delta S_{\text{column}}) \times 100 \tag{19}$$

$$\Delta S_C \% = (\Delta S_C / \Delta S_{\text{column}}) \times 100 \tag{20}$$

$$\Delta S_{\text{section\_flow}} \% = [(\Delta S_{\text{section\_flow}} - S_{FE} - S_F) / \Delta S_{\text{column}}] \times 100 \tag{21}$$

2.2. Distillation Column Feasibility Assessment. A sensitivity analysis was carried out to assess the parameter influence on the entropy balance of the extractive distillation column. The parameters studied are reflux ratio R, entrainer/feed flow rate ratio F_E/F, physical state q of the main and entrainer feed ($q = 1$ means at boiling temperature; $q = 0$ means at saturated vapor temperature), and the entrainer feed tray N_{FE} and main feed tray N_F. The reference temperature T_0 is set at 298.15 K.

On the basis of Figure 1a, the entropy balance of the column section alone, without reboiler and condenser, is analyzed first; the entropy balance of the column with external flows at a boiling temperature and at the reference temperature T_0 are studied subsequently.

We consider two azeotropic systems belonging to different Serafimov's class 1.0-1a, corresponding to the separation of a minimum-boiling azeotropic mixture acetone (A)−methanol (B) using a heavy entrainer water (E), and class 1.0-2, corresponding to the separation of the maximum-boiling azeotropic mixture acetone (A)−chloroform (B) using a heavy entrainer benzene (E). For the latter we investigated two subcases: case I when acetone can be obtained as distillate product and case II when chloroform is expected to be the distillate product.

The thermodynamic properties are computed using the modified (Dortmund) UNIFAC thermodynamic model.[23]

Table 1 lists the specifications of the columns to be studied. The number of trays N and main feed composition x_F are considered to be constant, and operating pressure is set at 1 atm.

Table 1. Column Specifications for Separation of the Azeotropic Mixtures of Acetone (A)−Methanol (B)−Water (E) and Acetone (A)−Chloroform (B)−Benzene (E).

specifications	class 1.0-1a	class 1.0-2 case I	class 1.0-2 case II
number of trays, N	60	30	30
entrainer feed tray, N_{FE}	20	10	10
feed tray, N_F	45	20	20
reflux ratio, R	2.76	5	5
entrainer feed flowrate, F_E	0.55	0.9	1.1
feed flowrate, F	1	1	1
feed composition			
x_A, mole fraction	0.5	0.9	0.1
x_B, mole fraction	0.5	0.1	0.9
entrainer composition			
x_B, mole fraction	0	0	0.3
x_E, mole fraction	1	1	0.7
distillate composition			
x_{DA}, mole fraction	0.956	0.986	0.998
x_{DB}, mole fraction	0.026	0.014	0.002
x_{DE}, mole fraction	0.018	0	0

We assume (i) there is no significant pressure gradient in the system, (ii) heat is supplied by the reboiler and lost in the condenser, and (iii) the column is adiabatic.

On the basis of a MESH equilibrium distillation column model, simulation using ProSimPlus 3.1 software[24] was carried out. Considering R, F_E/F, and composition as constants, those simulations provide the exact composition profiles, flow profiles, and temperature profile required for entropy calculations.

Many studies have been carried out for the class 1.0-1a system of acetone−methanol−water. The reflux ratio R and the values of F_E/F are taken from Knapp et al.[25,26] They proposed a minimum reflux ratio for the feasibility of continuous process at target product purity; the optimal operational parameters $R = 2.76$ and $F_E/F = 0.55$ are suggested on the basis of their flowsheet simulation.[25] For the class 1.0-2 corresponding system of acetone−chloroform−benzene, the operating parameters are set to make the process feasible; further optimization is out of our present objective. Depending on the expected distillate, either A or B, the overall column feed $x_F + x_E$ composition point is located in a different region of Figure 2; each of them are able to obtain either A or B (Table 1). For case II, the entrainer feed is not pure because that would lead to an unfeasible process under given values of x_D, R, and F_E.[16−18]

The feasibility of extractive distillation processes with a heavy entrainer for 1.0-1a and 1.0-2 classes has been studied in the literature[16,18,19,26−29]. According to the aforementioned works, feasibility is assessed by looking at the volatility order regions, univolatility curves, and topological characters of the residue curve map. Figure 2 displays the residue curve map of both systems.

In application of the general criterion for extractive distillation for 1.0-1a class,[16] the product A (acetone) is recovered in the distillate because it is located in the region where acetone is the most volatile and there exists a residue curve going from the entrainer vertex E to A in the direction of decreasing temperatures. For the 1.0-1a class, a minimum F_E/F is required to set at the point of stable extractive node near the E−A edge to make the separation feasible. For class 1.0-2, the feasibility criterion allows both A and B to be recovered depending on the location of the univolatility line $\alpha_{AB} = 1$; there is no entrainer flow
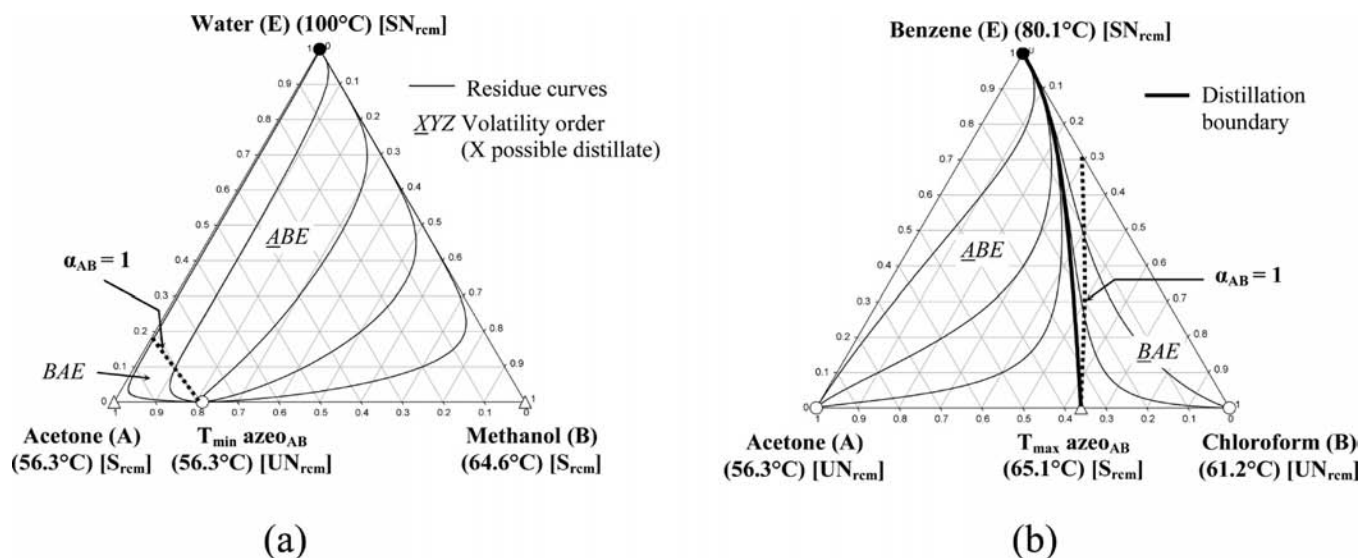
Figure 2. Residue curve map and univolatility line $\alpha_{AB} = 1$: (a) minimum-boiling azeotropic mixture acetone (A)−methanol (B) with heavy entrainer water (E) (class 1.0-1a); (b) maximum-boiling azeotropic mixture acetone (A)−chloroform (B) with heavy entrainer benzene (E) (class 1.0-2).
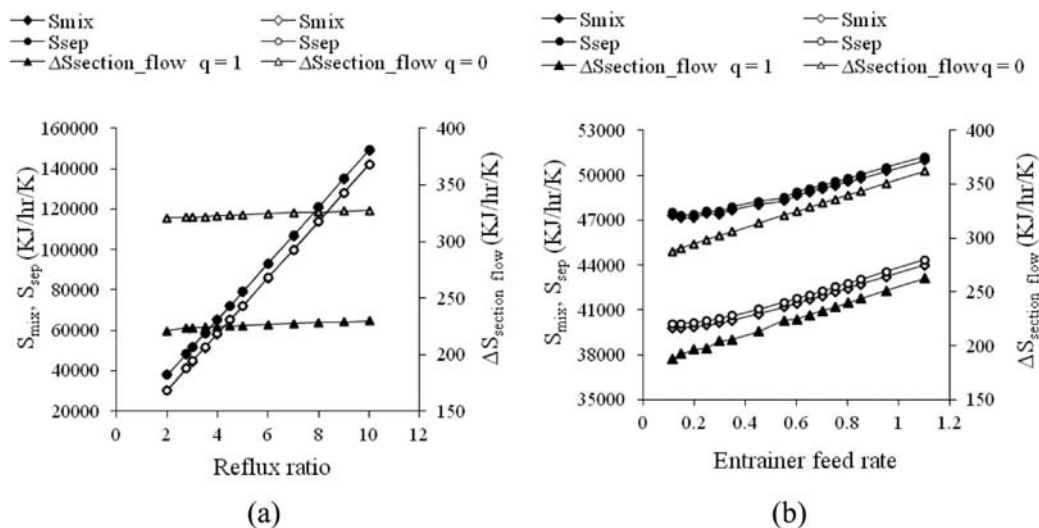

Figure 3. Entropy production without considering reboiler and condenser for the system of acetone−methanol−water at boiling liquid ($q = 1$) and saturated vapor feed states ($q = 0$) as a function of (a) reflux ratio at $F_E/F = 0.55$ and (b) as a function of F_E/F at $R = 2.76$.
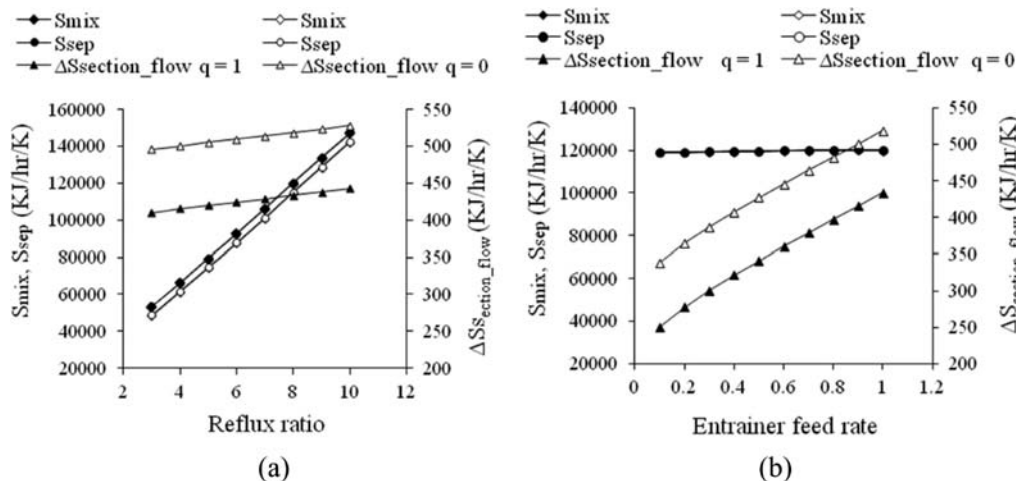

Figure 4. Entropy production in the column section without reboiler and condenser for the system of acetone−chloroform−benzene (case I) as a function of (a) reflux ratio at $F_E/F = 1$ and (b) as a function of F_E/F at $R = 8$.
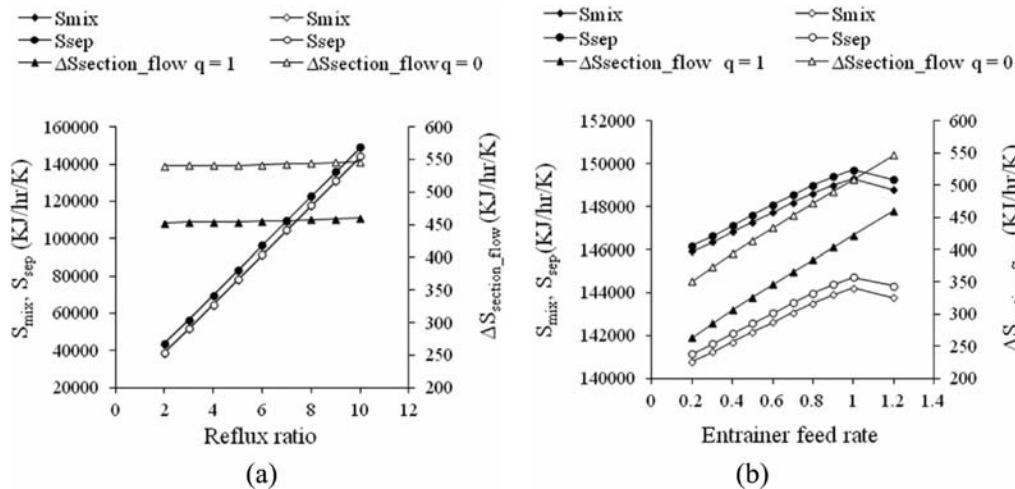
Figure 5. Entropy production in the column section without reboiler and condenser for the system of acetone−chloroform−benzene (case II) as a function of (a) reflux ratio at $F_E/F = 1.2$ and (b) as a function of F_E/F at $R = 10$.
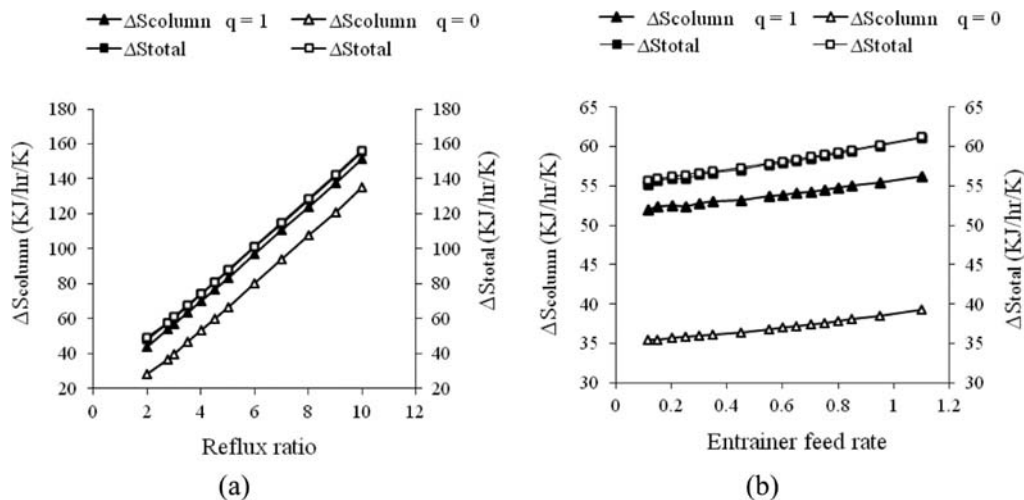

Figure 6. Entropy production in the extractive distillation process as function of (a) the reflux ratio at $F_E/F = 0.55$ and (b) as a function of F_E/F at $R = 2.76$.

rate limit to recover product A (acetone), but there exists a maximum entrainer flow rate to recover B (chloroform) because of the intersection of the univolatility line with the B−E edge.

For the class 1.0-1a system of acetone−methanol−water, at the fixed $F_E/F = 0.55$, the reflux ratio is varied in the range of 2−10. At the fixed $R = 2.76$, the F_E/F is varied in the range of 0.11−1.20. The entrainer feed temperature ranges from 298.15 to 373.15 K (boiling liquid). The main feed temperature ranges from 308.15 K to a temperature slightly above its saturated vapor feed temperature 330.3 K. The position of the entrainer feed tray is varied by keeping $N_F = 45$. Then, the position of the feed tray is varied by keeping $N_{FE} = 10$

For the two cases of class 1.0-2 corresponding to acetone−chloroform−benzene, the reflux ratio R is varied in the range of 2−10 at fixed F_E/F. The F_E/F is varied in the range of 0.2−1.2 at the fixed reflux ratio. The entrainer feed temperature ranges from 298.15 to 353.28 K (boiling liquid temperature). The total number of trays is first fixed at 30; feed tray is considered to be 20, and the entrainer feed tray is correspondingly varied. The total number of trays is varied by setting the entrainer and feed trays as 10 and 20, respectively.

3. RESULTS AND DISCUSSION

3.1. Column Section without Reboiler and Condenser.
Figures 3−5 illustrate the evolution of the entropy production, $\Delta S_{section\_flow}$, in the column section excluding the reboiler and condenser for two thermal feed states ($q = 0$ and $q = 1$). In view of the fact that the entropy of mixing S_{mix} is almost indistinguishable from entropy of separation S_{sep}, their difference $\Delta S_{section\_flow}$ is shown on the right axis.

The analysis of the results shows that at a fixed F_E/F rate, the entropy of mixing S_{mix} and entropy of separtion S_{sep} increase significantly. The entropy production is the difference between S_{sep} and S_{mix} in the column section; $\Delta S_{section\_flow}$ increases with the increase in reflux ratio as shown in Figures 3a, 4a, and 5a. At a fixed R, the entropy of mixing S_{mix} and entropy of separtion S_{sep} increase slightly. The entropy production in the column section $\Delta S_{section\_flow}$ increases with the increase in F_E/F (Figures 3b, 4b, and 5b), and the extent of increase is more significant than that of the reflux ratio.

3.2. Extractive Column and Extractive Distillation Process.
The entropy production of the column section with condenser and reboiler ΔS_{column} and the total entropy production of the whole process, namely the whole column and the inflow

Figure 7. Entropy production in the extractive distillation (case I) as function of (a) the reflux ratio at $F_E/F = 1$ and (b) as a function of F_E/F at $R = 8$.

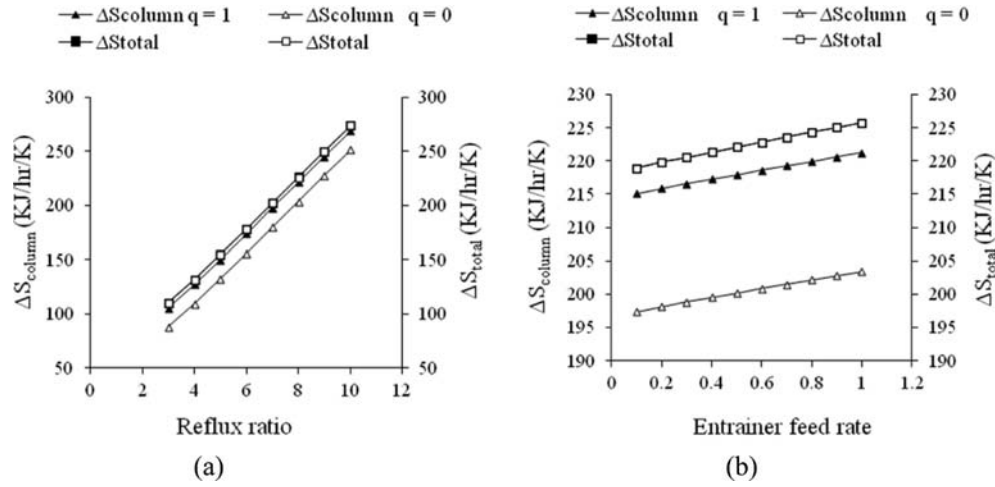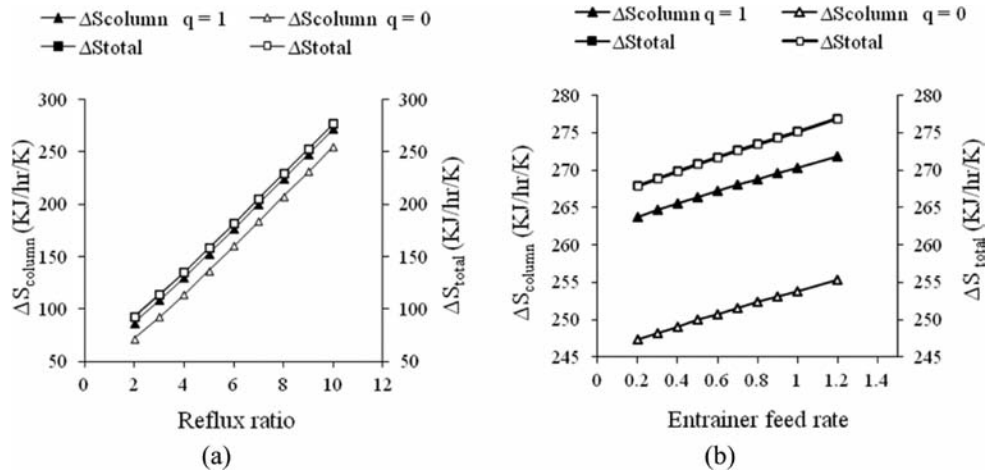
Figure 8. Entropy production in the extractive distillation (case II) as function of (a) the reflux ratio at $F_E/F = 1.2$ and (b) as a function of F_E/F at $R = 10$.

and outflow preheater and postcooler ΔS_{total}, are plotted as a function of reflux ratio and F_E/F in Figures 6–8.

We note that both ΔS_{column} and ΔS_{total} increase significantly with the increase in R; however, only a slight increase is observed because of the increase in F_E/F. In addition, the R increase leads to an increase of the entropy production in the column section that is greater than that of the F_E/F increase because of the augmentation of internal flows in the column section. At fixed reflux ratio, the internal liquid flowrate remains constant at the rectifying section of the column and varies moderately along the extractive and stripping sections with F_E/F. For class 1.0-1a, within the range of F_E/F from 0.1 to 1.1, the internal liquid flowrate varies from 1.441 to 2.464 kmol/h at the entrainer feed stage and from 2.399 to 3.418 kmol/h at the main feed stage. On the other hand, at fixed solvent rate, the internal liquid flowrate varies at the top of the column along with the reflux ratio. Within the range of reflux ratio from 2 to 10, the internal liquid flowrate varies from 1 to 5 kmol/h at the top of the column, from 1.513 to 5.423 kmol/h at the entrainer feed stage, and from 2.478 to 6.255 kmol/h at the main feed stage. For class 1.0-2, we notice the same behavior of internal flowrates along the extractive distillation column. Therefore, in order to make separation of azeotropic mixtures possible by extractive distillation with less entropy production, we recommend increasing the entrainer feed ratio and reducing the reflux ratio as low as possible.

The feed state significantly affects the extractive column entropy separation ΔS_{column}. This happens because a boiling liquid feed has to be vaporized in the reboiler, whereas a saturated vapor feed does not, as ΔS_B values show in Table 2.

As expected, the feed state does not significantly affect the total entropy ΔS_{total}. This can be explained by the fact that the entropy production is computed with respect to the reference temperature T_0 for the whole process with heater and cooler. In the case of saturated vapor feed, if an ideal mixture is fed, the extra heat that is needed to vaporize the feed would be equivalent to the

Table 2. Entropy Production in the Column Section, Reboiler, and Condenser As Function of Thermal Feed State of System 1.0-1a for $R = 2.76$ and $F_E/F = 0.55$ and of System 1.0-2 for Case I at $R = 5$ and $F_E/F = 0.9$ and for Case II at $R = 5$ and $F_E/F = 1.1$ (in Kilojoules per Hour-Kelvin)

case	thermal feed state	$\Delta S_{section\_flow}$	ΔS_C	ΔS_B	S_{FE}	S_F
1.0-1a	$q = 1$	223.54	19.45	28.61	38.53	179.32
	$q = 0$	321.09	19.50	12.42	38.53	277.68
1.0-2	$q = 1$	401.82	51.95	68.89	155.93	217.49
case I	$q = 0$	486.91	51.96	56.65	155.93	308.11
1.0-2	$q = 1$	435.18	57.82	80.62	202.37	218.94
case II	$q = 0$	522.19	57.71	66.34	202.37	307.92

extra heat that was provided in the reboiler for the case of boiling the liquid feed; while those two heats are not equal to those for a nonideal mixtures, the difference remains small compared to the latent heat of vaporization of the feed. Accordingly, regardless of the thermal feed state when distillate and bottom products are cooled to room temperature, the entropy production varies very slightly, but the value is larger than that when the products are withdrawn to their bubble points. Therefore, we recommend extractive distillation process with vapor main feed state and recovered products at boiling temperature.

Heat flow and energy efficiency of the extractive distillation process as a function of reflux ratio and entrainer/feed ratio are analyzed. One of the means of reducing energy consumption in the distillation process is to decrease the heat supplied to the reboiler. The minimum power input for separating a mixture into the required products is usually quite small in relation to the actual heat input; therefore, the efficiency of the separation process is low. In this section, we compute the minimum work and the lost work for both mixtures in different thermal feed states. Results for the system of acetone−methanol−water are presented in Table 3 and illustrated in Figure 9. For a system of acetone−chloroform−benzene, the main results are indicated in Table 3 and displayed in Figures 10−11.

Table 3. Heat Flow of the Column for System 1.0-1a at $R = 2.76$ and $F_E/F = 0.55$ and for System 1.0-2 case I at $R = 5$ and $F_E/F = 0.9$ and case II at $R = 5$ and $F_E/F = 1.1$ (in Kilojoules per Hour).

case	thermal feed state	Q_C	Q_B	Q_{loss}	W_{min,T_0}
1.0-1a	$q = 1$	56445	59010	17215	575.38
	$q = 0$	56499	25990	17250	602.00
1.0-2 case I	$q = 1$	160014	166871	45828.6	176.80
	$q = 0$	160015	137246	45831.6	178.90
1.0-2 case II	$q = 1$	159664	166919	46905.0	92.59
	$q = 0$	159667	137424	46928.8	115.80

We can see that at a fixed entrainer/feed ratio, the minimum isothermal work for the system acetone−methanol−water shows a minimum reflux ratio close to 3.5. However, the energy loss steadily increases along with the reflux ratio. This can be observed for both thermal feed states (Figure 9a). At a fixed reflux ratio, for investigated thermal states of feed, both the minimum isothermal separation work and the enthalpy separation increase steadily with the entrainer/feed ratio. For LW, this increase is smaller than that of the case in Figure 9a. These results indicate that a reversible separation should be run at a reflux ratio of 3.5. Although not exactly the same as the optimal design result reported in the literature, this value of reflux ratio is within the range of the literature recommendation.[26,30,31]

For the mixtures of class 1.0-2, Figure 10 suggests that an irreversible separation in lower degree should be run at a reflux greater than 6, and the entrainer flow rate should be set as low as possible (subcase I) or as high as possible (subcase II).

Considering the fact that the enthalpy of separation represents the difference between the heat supplied to the reboiler and that recovered from the condenser $(Q_B - Q_C)$, Figure 12 shows a maximum at a reflux ratio of 3.5 and a steady increase with the entrainer flow rate for class 1.0-1a. The enthalpy difference is more influenced by reflux ratio than by the value of F_E/F. The amount of heat loss varies slightly when the feed is introduced to the column at the saturated vapor state $(q = 0)$.

Figure 13 displays that $(Q_B - Q_C)$ is slightly influenced by the reflux ratio, whereas the increase in F_E/F has an appreciable effect on this enthalpy difference.

The entropy production of system 1.0-2 at different operating conditions for distillate purity of 99% acetone for case I and chloroform for case II are given in Table 4.

3.3. Effect of Phase in the Main Feed. Concerning the thermal state of the main feed (the entrainer being fed as boiling liquid), $\Delta S_{section\_flow}$ is more important for a saturated vapor feed state than for a boiling liquid feed state. This is because, for a saturated vapor feed, the entropy inside the column section already incorporates the entropy contribution of the preheating of the feed to its saturated vapor state that is effectively noticed in the S_F value (Table 2). In parallel, the reboiler entropy ΔS_B is lower as no extra heat is required in the reboiler to vaporize the saturated vapor feed (Table 2). The entropy production and irreversibility of the column as a function of thermal feed state for the systems of classes 1.0-1a and 1.0-2 for given operational parameters are presented in Table 5.

The entropy production percentage generated in the reboiler, condenser, and tray column are computed from the entropy balance eqs 19−21 and reported in Table 6.

As shown in Table 6, for a distillation process, the reboiler percentage dominates, followed by the condenser and the column section. This can be explained by the fact that the change
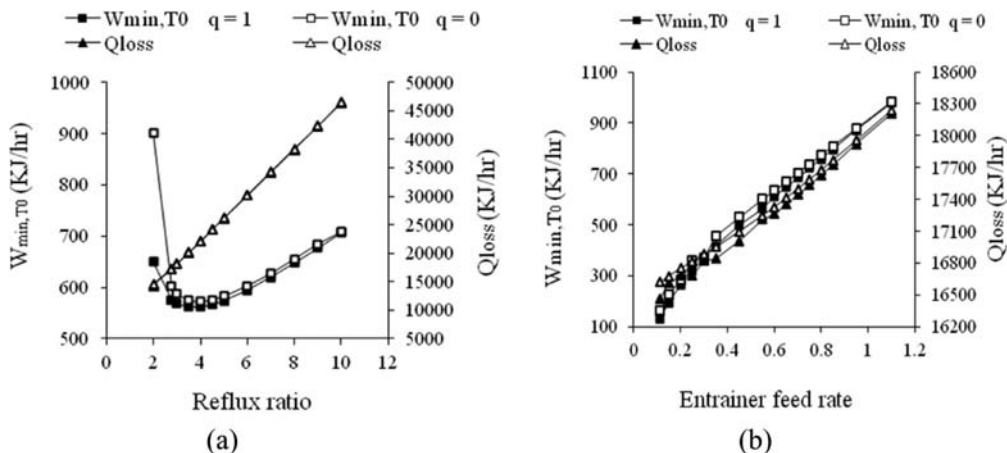

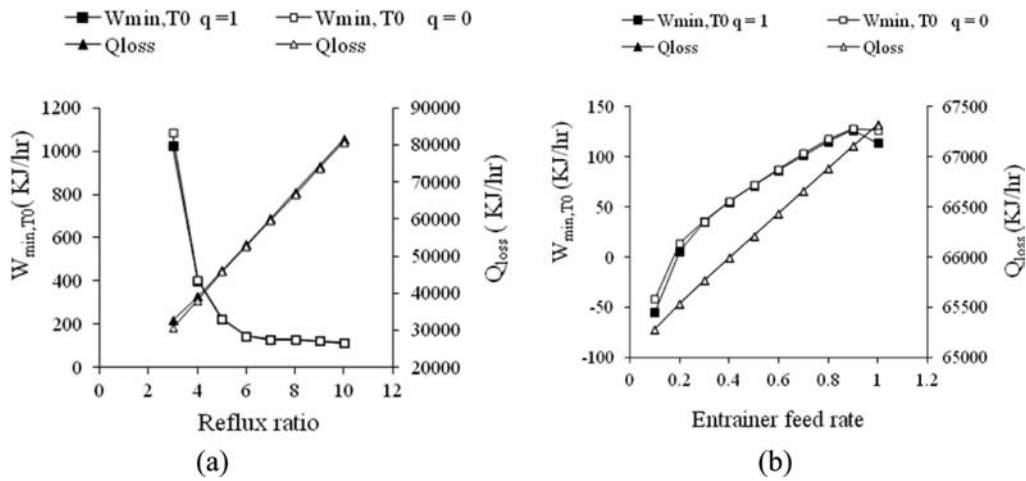Figure 9. Minimum work and lost work for system 1.0-1a as a function of (a) reflux ratio and (b) F_E/F.

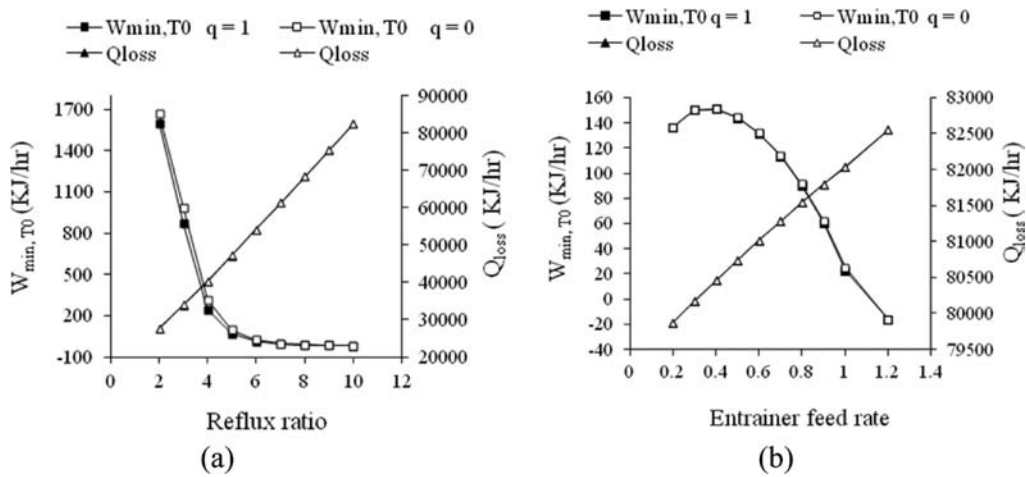**Figure 10.** Minimum work and lost work for system 1.0-2 case I as a function of (a) reflux ratio and (b) F_E/F.

Figure 11. Minimum work and lost work for system 1.0-2 case II as a function of (a) reflux ratio and (b) F_E/F.
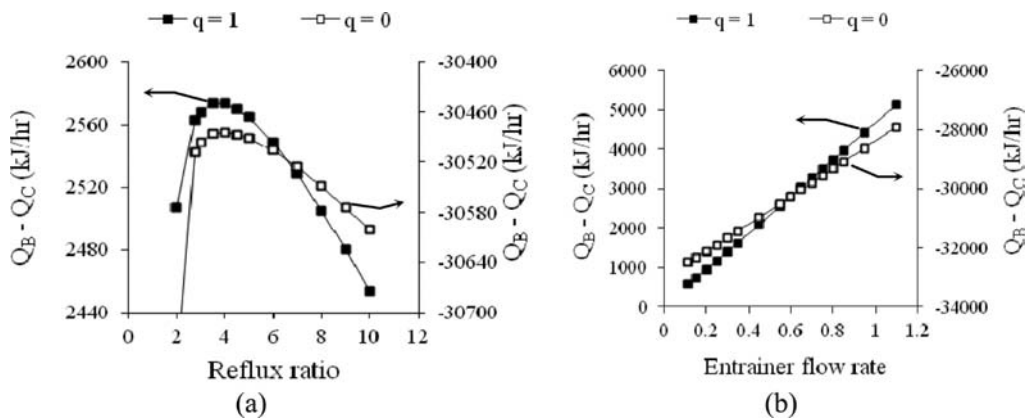

Figure 12. Enthalpy of separation $(Q_B - Q_C)$ for system 1.0-1a as a function of (a) reflux ratio and (b) entrainer/feed flow ratio for the system acetone–chloroform–benzene 1.0-2.

in temperature in the reboiler and condenser is greater than that in the column.

The fact that the reflux ratio R should be as low as possible is also validated by entropy production analysis. Indeed, R increases the internal flows inside the column and thus the energy required in both the energy exchanges inside the column and vaporization in the reboiler. Those in turn sharply increase the entropy. Similarly, F_E/F should be kept as low as possible, but above the

minimum value for feasibility (1.0-1a). However, it is important to keep it less than R. It impacts moderately the total entropy production ΔS_{total}. Finally, the main feed state has no influence on ΔS_{total} and there is no incentive to promote either a boiling liquid or a saturated vapor state to reduce the process irreversibility.

It was expected that the liquid and vapor entropy flow profiles would have the same tendency as those of liquid and vapor flows
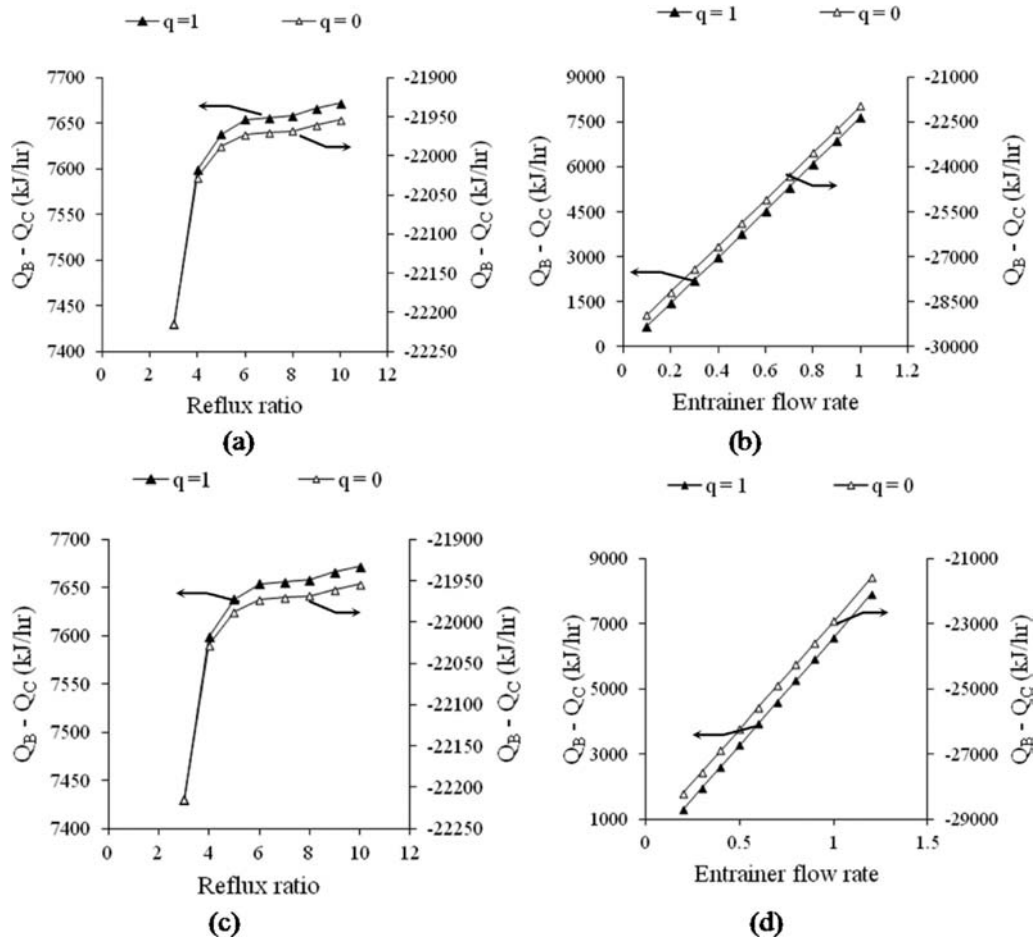
Figure 13. Enthalpy of separation $(Q_B - Q_C)$ as a function of reflux ratio and entrainer/feed flow ratio for system 1.0-2 for (a, b) case I and (c, d) case II.

Table 4. Entropy Production in Extractive Distillation Process of System 1.0-2 at Different Operating Conditions (in Kilojoules per Hour-Kelvin)

case	R	F_E/F	x_D	ΔS_C	ΔS_B	$\Delta S_{section\_flow}$	ΔS_{column}	ΔS_{total}
1.0-2 case I	5	0.9	0.9856	51.95	68.89	401.82	149.23	153.71
	6	0.8	0.9860	60.58	80.28	387.61	172.36	176.75
	8	0.7	0.9863	68.87	91.17	392.24	219.27	223.59
1.0-2 case II	5	1.1	0.99	57.82	80.62	435.18	152.31	157.32
	6	1.0	0.99	67.26	93.42	417.44	175.20	180.11

Table 5. Entropy Production and Irreversibility of System 1.0-1a at R = 2.76 and F_E/F=0.55 and of System 1.0-2 for Case I at R = 5 and F_E/F = 0.9 and for Case II at R = 5 and F_E/F = 1.1

cases	thermal feed state	entropy production (kJ/(h K))				irreversibility (kW)	
		ΔS_{column}	ΔS_{heater}	ΔS_{cooler}	ΔS_{total}	I_{column}	I_{total}
1.0-1a	$q = 1$	53.75	3.03	0.96	57.74	4.45	4.78
	$q = 0$	36.80	20.11	0.95	57.86	3.05	4.79
1.0-2 case I	$q = 1$	149.23	3.21	1.27	153.71	12.36	12.73
	$q = 0$	131.47	20.98	1.27	153.72	10.89	12.73
1.0-2 case II	$q = 1$	152.31	3.06	1.95	157.32	12.61	13.03
	$q = 0$	135.95	19.49	1.96	157.40	11.26	13.04

in the extractive distillation column. The entropy of mixing and the entropy of separation vary moderately along the extractive and rectifying sections, while they change significantly in the stripping section irrespective of the thermal feed state. Furthermore, the lower values of the entropy flows are obtained in the case of a saturated vapor feed state. This can be explained by the decrease in the energy supplied to the reboiler and

increase of the temperature in the stripping section for each investigated thermal feed state.

Figures 14−16 show the entropy production on each tray $\Delta S_{column,j}$ and the temperature profile. The temperature profiles for class 1.0-1a are similar to those published by Luyben et al.[30]

The entropy production profiles show that the entropy is mostly generated at the entrainer feed tray, at the main feed tray,

Table 6. Entropy Production Percentage Generated in the Reboiler, Condenser, and Trayed Column

system	thermal feed state	entropy production (%)			temperature (K)	
		column section	condenser	reboiler	T_B	T_C
1.0-1a	$q = 1$	10.59	36.17	53.23	344.11	329.15
	$q = 0$	13.26	33.75	52.98	343.86	329.11
1.0-2	$q = 1$	19.02	34.81	46.16	351.11	329.45
case I	$q = 0$	17.39	39.52	43.09	351.08	329.47
1.0-2	$q = 1$	9.10	37.96	52.93	347.01	334.39
case II	$q = 0$	8.76	42.45	48.79	347.01	334.41

and at the reboiler (Figures 14a–16a), and it results from the mixing of entrainer and feed flows with the internal column's flows. For both systems of classes 1.0-1a and 1.0-2, the temperature profiles increase from the top to the bottom of the column. We note that the thermal feed state has less effect on temperature profile for both investigated systems.

3.4. Effect of Entrainer and Feed Temperatures on the Entropy Production of the Extractive Distillation Process. In this section, we investigate the influence of the entrainer and feed temperatures on the entropy production of the extractive process.

Figures 17a and 18a show that the entropy production of the column ΔS_{column} is reduced with the increase of the entrainer feed temperature, whereas the total entropy production, ΔS_{total}, does not change. In Figure 18a, ΔS_{total} decreases as the entrainer temperature increases. This quantity is lower in the case of the saturated vapor feed state compared to that in the case of saturated liquid feed state for the same reason as mentioned before. These trends are not significant and there is no true recommendation for setting the entrainer feed temperature.

Figure 17b shows that the entropy production in the column for class 1.0-1a decreases steadily as the feed temperature increases in a liquid, and it drops significantly when the feed vaporizes. There is a very steep decrease during vaporization because the bubble and dew temperature difference of the equimolar feed is only 0.89 K. The steady decrease would mean that it is advantageous to introduce the feed at a saturated vapor state. However, when considering the process as a whole with the preheater and postcooler, ΔS_{total} remains constant and again there is no true recommendation for setting the main feed temperature.

3.5. Influence of the Feed Trays Position on the Entropy Production of the Column. Finally, the effect of the entrainer and main feed tray positions on the entropy production is evaluated at a fixed total number of trays. That affects the extractive section length and could affect process feasibility or at least the product purity. However, for the case of class 1.0-1a, the process feasibility is rather dominated by the entrainer flow rate that should be above a minimum value.[16] The results are displayed in Figure 19.

The column entropy production, ΔS_{column}, changes moderately and reaches a minimum value at $N_{FE} = 20$, while the mole fraction of acetone in the distillate reaches a maximum of 0.956. The longer the extractive section, the closer the ending point of the extractive section to the water–acetone edge in the triangle graph; thus, the rectifying section composition is able to reach a point with higher acetone purity.

The column entropy production decreases as a function of the main feed tray position and the mole fraction of acetone in the distillate and increases when the number of stages in the extractive section increases near to stages 20 at the purity of 0.956 (Tables 7 and 8).

For system 1.0-2 case II (Table 8), we notice a behavior opposite that in Figure 19a for the system of class 1.0-1a as there is a minimum in distillate composition corresponding to a maximum in ΔS_{column} increase as the entrainer feed tray is changed. This may be related to the length of the column sections as this minimum appears when the three sections of the column have the same lengths (Figure 20).

For system of class 1.0-2, we observe that in both case I and case II, the entropy production ΔS_{column} as a function of entrainer feed tray decreases and the total entropy product ΔS_{total} increases as the total tray column number increases. This is due to the increase of the stripping section and the increase of the mole fraction of product in the distillate. For all three cases, the higher the product purity, the smaller the heat loss.

4. CONCLUSIONS

The entropy production of the extractive distillation column was analyzed for the separation of a minimum- and maximum-boiling azeotropic mixture by using a heavy entrainer (Serafimov's classes 1.0-1a and 1.0-2) by varying the reflux ratio, entrainer/feed ratio, and the temperatures of entrainer and main feed.
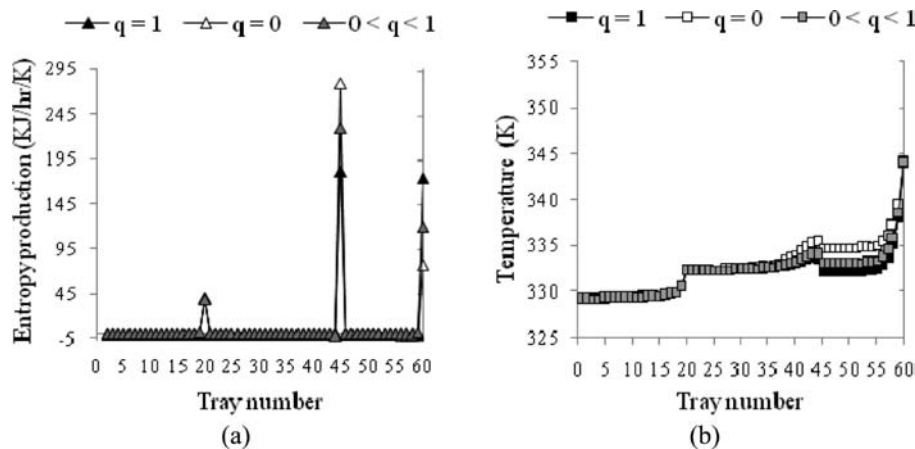

Figure 14. (a) Entropy production profile and (b) temperature profile of the column operating at $R = 2.76$ and $F_E/F = 0.55$ of class 1.0-1a system.
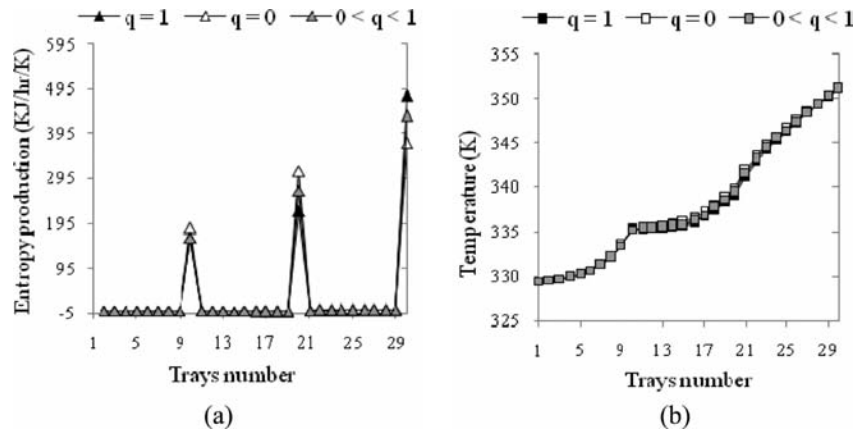
Figure 15. (a) Entropy production profile and (b) temperature profile of the column operating at $R = 5$ and $F_E/F = 0.9$ of class 1.0-2 case I system.
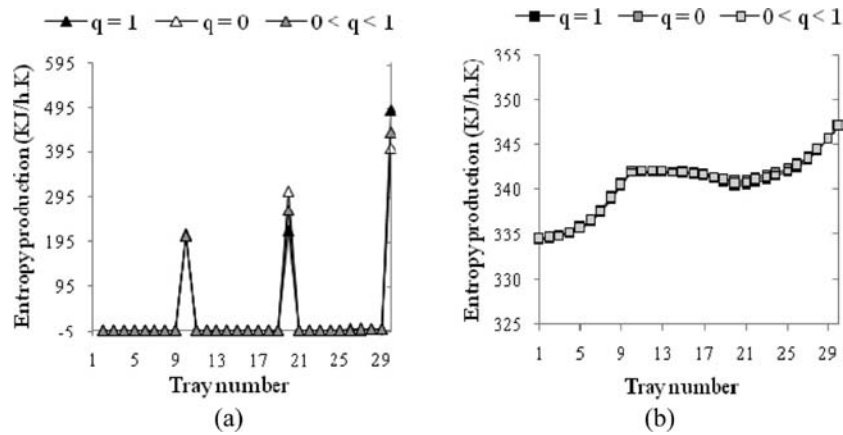

Figure 16. (a) Entropy production profile and (b) temperature profile of the column operating at $R = 5$ and $F_E/F = 1.1$ of class 1.0-2 case II system.
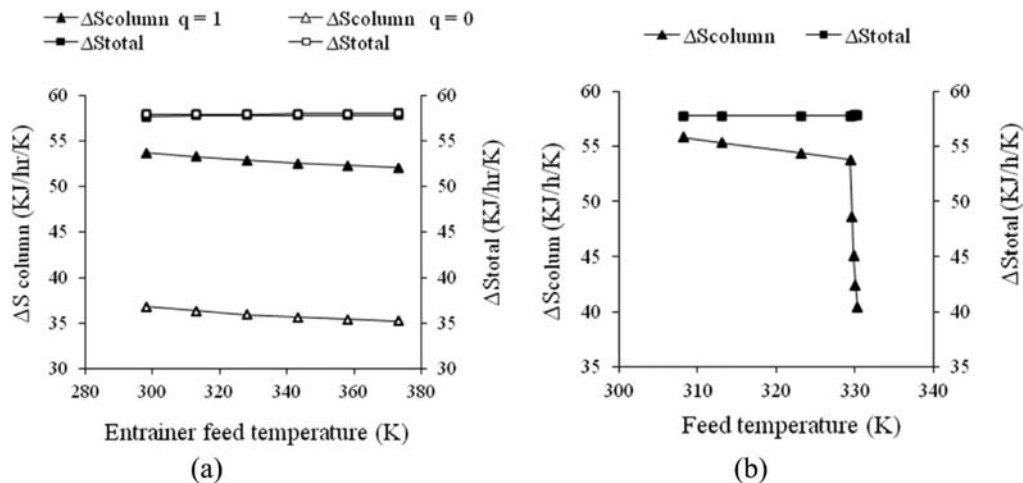

Figure 17. Entropy production of the column and the extractive distillation process for system of class 1.0-1a at $R = 2.76$ and $F_E/F = 0.55$ as a function of (a) entrainer feed temperature for boiling main feed and for saturated vapor main feed and (b) feed temperature at $T_{FE} = 298.15$ K.

Most of the entropy is generated in the reboiler and condenser because of the temperature changes at the feeding points of the entrainer and main feed because of the irreversibility of mixing.

Increasing the reflux ratio increases the entropy production of the process because of the rise of the internal flows. The F_E/F ratio has a similar but smaller effect on the entropy generation of the column.

The effect of mixing in the column section on the entropy production is more significant with increase in the reflux ratio

than with increase in F_E/F. Therefore, to reduce the entropy production and hence the energy consummation, we recommend maintaining the reflux as low as possible and increasing the solvent rate as much as possible to achieve the required purity.

Increasing the temperature of the main feed or the entrainer feed, both kept as liquids, reduces the entropy production of the whole column (sections with reboiler and condenser) and its irreversibility because it lowers the reboiler heat and entropy. When considering the whole process with inflows and outflows at
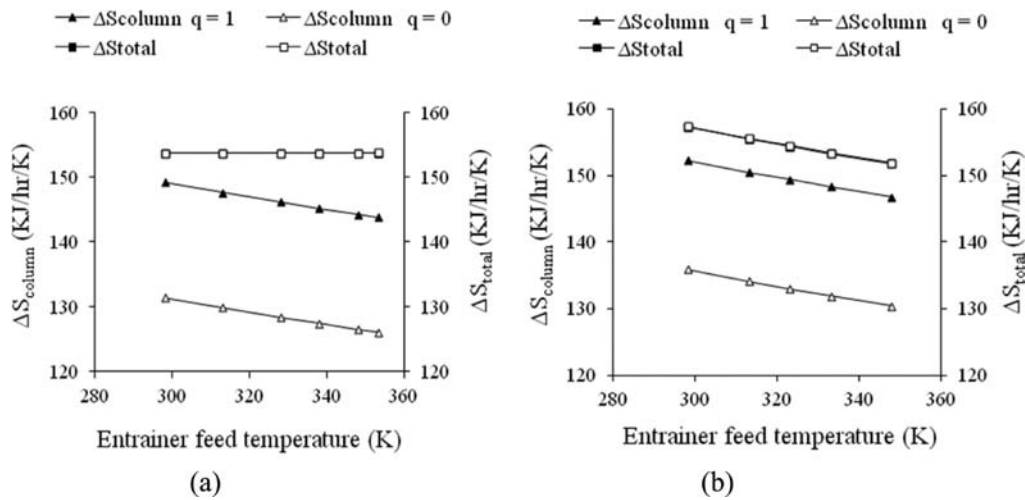
Figure 18. Evolution of entropy production as a function of entrainer feed temperature for system of class1.0-2 for (a) case I at $R = 5$ and $F_E/F = 0.9$ and (b) case II at $R = 5$ and $F_E/F = 1.1$.
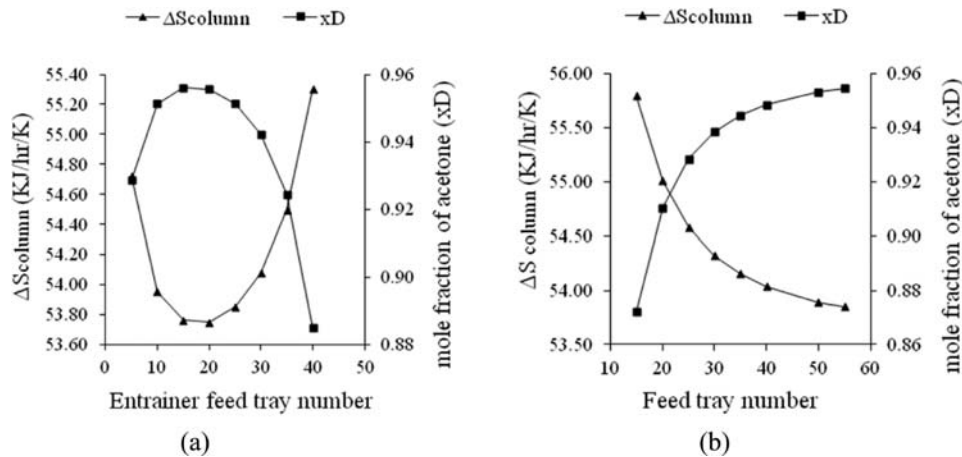

Figure 19. Entropy production and mole fraction of acetone separated in distillate for system 1.0-1a: (a) the entrainer feed stage position; (b) the main feed stage position.

Table 7. Entropy Production as a Function of Entrainer Feed Tray for System 1.0-2 (Case I) at $R = 5$ and $F_E/F = 0.9$

N_{FE}	x_D	ΔS_{column} (kJ/(h K))	ΔS_{total} (kJ/(h K))	Q_{loss} (kJ/h)
5	0.9277	152.43	154.25	45990.3
10	0.9856	149.23	153.71	45829.7
15	0.9878	149.08	153.57	45785.4

Table 8. Entropy Production as a Function of Entrainer Feed Tray for System 1.0-2 (Case II) at $R = 5$ and $F_E/F = 1.1$

N_{FE}	x_D	ΔS_{column} (kJ/(h K))	ΔS_{total} (kJ/(h K))	Q_{loss} (kJ/h)
5	0.9903	152.31	157.32	46903.5
10	0.9673	153.60	158.63	47295.8
15	0.9926	152.11	157.12	46845.6

the reference temperature, the feed temperature effect is negligible. The same can be said when the main feed vaporizes. Therefore, determination of an optimum value for setting the main feed temperature cannot be made here. That decision should be taken at the plant flowsheet level, where pinch analysis for energy integration could rule out the transfer of heat to the reboiler in favor of a preheating of the feed.

Computing the minimum isothermal work in order to find the less irreversible design, an optimal reflux $R = 3.5$ is found for class 1.0-1a, whereas R should be higher than 6 for the two subcases of class 1.0-2. However, the real irreversible separation has no such optimum as the energy loss always steadily increases with either the reflux or the entrainer flow rate for the systems of class 1.0-1a and two subcases of class 1.0-2.

Finally, the entropy generation is sensitive to feed tray positions of both the entrainer and main feed. No recommendation is clear, but they evidently affect the product purity through the length of each column section. It is noticed that for all three cases, the higher the product purity, the smaller the energy loss.

This work shows how entropy generation is sensitive to many design and operating parameters of the extractive distillation process. This work should help engineers to operate the process at an optimal set of parameters, reducing the energy loss.

The analysis of entropy generation carried out in this study is the starting point to define new operational strategies and design features that allow a more efficient use of energy. Future work is in progress to consider the process with the regeneration column and to investigate separations of azeotropic mixtures with light or intermediate boiling entrainers.
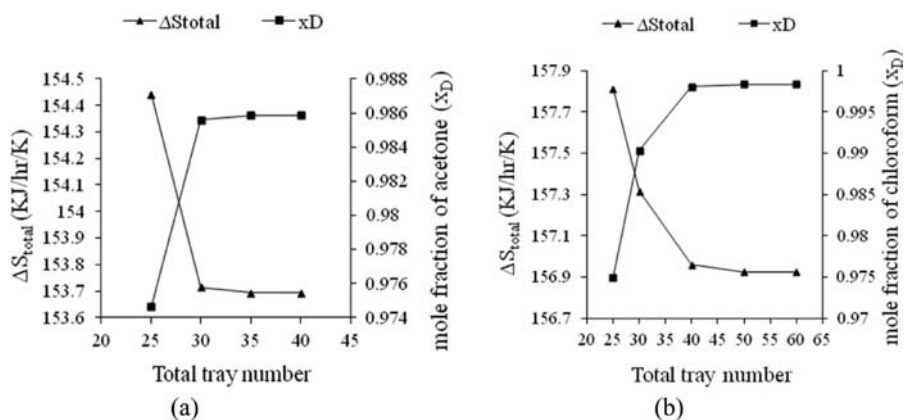
Figure 20. Entropy production and mole fraction of distillate product as function of the total tray number for system of class1.0-2 for (a) case I, acetone recovered in the distillate, and (b) case II, chloroform recovered in the distillate.

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Notes

The authors declare no competing financial interest.

■ NOMENCLATURE

Symbols

T = temperature, K

P = pressure, kPa

x = component molar fraction in liquid

y = component molar fraction in vapor

y^* = component molar fraction of vapor in equilibrium

x_E = component molar fraction of entrainer

x_D = component molar fraction of distillate

c_p = specific heat, kJ/(kmol K)

γ = activity coefficient

R = reflux ratio

F_E/F = entrainer/feed flow rate ratio

ΔS = entropy production, kJ/(h K)

Q = heat flow, kJ/h

N = total tray number

N_{FE} = entrainer/feed tray

N_F = main feed tray

W = bottoms flow rate, kmol/h

D = distillate flow rate, kmol/h

L = liquid flow, kmol/h

V = vapor flow, kmol/h

F = feed flow rate, kmol/h

H = molar enthalpy, kJ/kmol

W_{min,T_0} = minimum isothermal work

η = second law efficiency

q = mole fraction of liquid in the feed

Subscripts and Superscripts

i = referring to component i of the mixture

j = referring to distillation tray j

1 = top tray of the column section

n = last tray of the column section L − liquid

0 = standard conditions

L = liquid

V = vapor

E = entrainer

C = condenser

B = reboiler

surr = surrounding

mix = mixing

sep = separation

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