

## Second Law Analysis of Conventional and Nonconventional Distillation Sequences

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In this work thermodynamic efficiency calculations for the separation of ternary and quaternary mixtures of hydrocarbons in conventional, heat-integrated and thermally coupled distillation sequences, are presented. When a ternary mixture was considered, energy savings achieved in the thermally coupled and heat-integrated distillation sequences ranged from 10 to 40 % in comparison to conventional direct and indirect distillation sequences. Regarding thermodynamic efficiency, thermally coupled and heat-integrated distillation sequences presented the highest values in almost all of the cases considered. As the analysis was extended to the separation of quaternary mixtures, the thermally coupled distillation sequences show acceptable energy savings and the thermodynamic efficiency of a thermally coupled distillation sequence linked to a side stripper and a side rectifier was better than that obtained in the conventional distillation sequence; however, the second law efficiency for the thermally coupled distillation with prefractionator (Petlyuk-type column) was low, when compared to that of the conventional distillation sequence for a mixture with low content of intermediate components. When both thermal links and heat integration were introduced in the thermally coupled distillation sequence with side columns, the energy saving and second law efficiency increased too.

*Key words:*

Thermally coupled distillation, heat-integrated distillation, second law efficiencies

### Introduction

Distillation remains as one of the most widespread used separation methods despite its high energy demands on the reboilers. Nevertheless, the trend in process systems design is to include separation schemes that can provide significant energy and capital savings; for example, complex distillation sequences, such as thermally coupled (Figure 1) and heat-integrated distillation sequences (Figure 2), which can offer energy savings around 40 % for the separation of some multicomponents mixtures in contrast to conventional distillation trains (Figure 3) widely used in the chemical industry [Tedder and Rudd;<sup>1</sup> Triantafyllou and Smith;<sup>2</sup> Annakou and Mizsey<sup>3</sup> Hernández and Jiménez<sup>4</sup> and Jiménez et al.<sup>5</sup>].

Blancarte-Palacios et al.<sup>6</sup> and Christiansen et al.<sup>7</sup> have extended the ideas of thermally coupled separation to systems of quaternary mixtures. Those authors studied the conventional distillation sequence (CDS), the thermally coupled distillation sequence with a side stripper and a side rectifier (TCDS-SS/SR), and a Petlyuk-type column

(TCDS-PR) shown in Figure 4. Their results indicate that similar energy savings can be obtained when compared to the separation of ternary mixtures. Recently, Rong et al.<sup>8</sup> have reported additional energy savings including, both, thermal couplings and heat integration as indicated in Figure 5.

In this paper we calculate and compare second law efficiencies and energy consumption required to distill ternary and quaternary mixtures of hydrocarbons using the distillation sequences indicated in Figures 1 through 5.

### Design of the distillation sequences

The design and optimisation strategies of conventional distillation sequences are well-known (as described in the work of Seader and Henley<sup>9</sup>) and have been implemented in process simulators. In this work the conventional distillation sequences of Figures 3 and 4a were designed and optimised using the process simulator Aspen Plus 11.1<sup>TM</sup>. In the case of both thermally coupled distillation sequences of Figure 1, the design and optimisation

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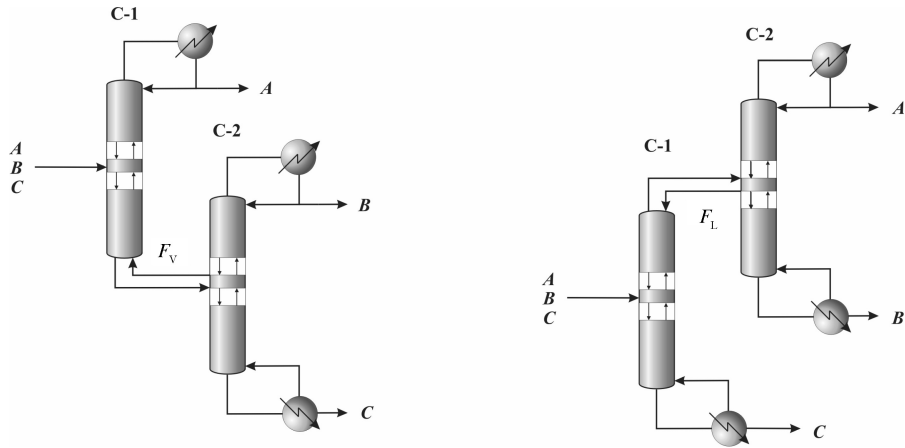


Fig. 1 – Thermally coupled distillation sequences for the separation of ternary mixtures: (a) Direct (TCDS-D), (b) Indirect (TCDS-I)

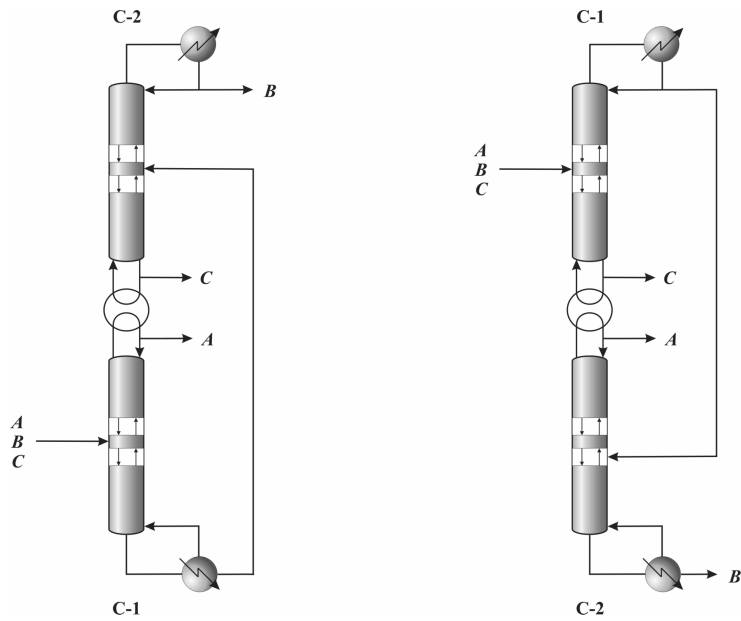


Fig. 2.– Heat-integrated distillation sequences for the separation of ternary mixtures: (a) Direct (DSI), (b) Indirect (ISI)

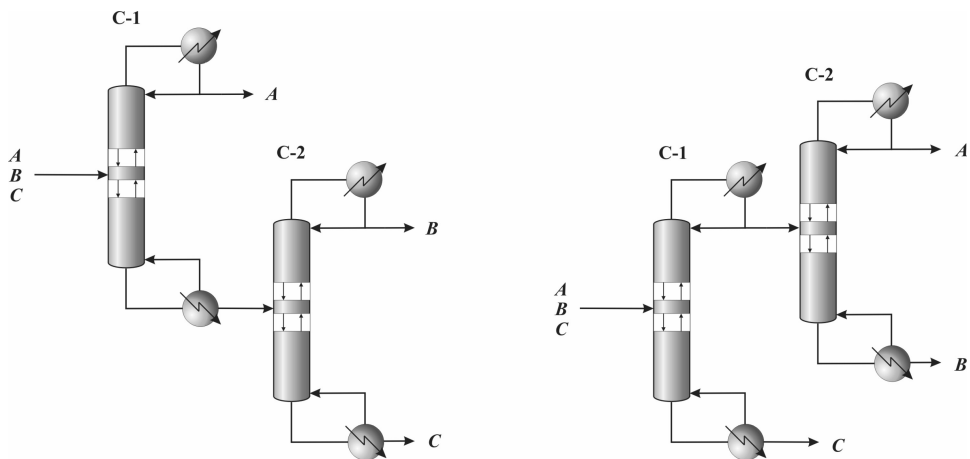


Fig. 3.– Conventional distillation sequences for the separation of ternary mixtures: (a) Direct (DS), (b) Indirect (IS)

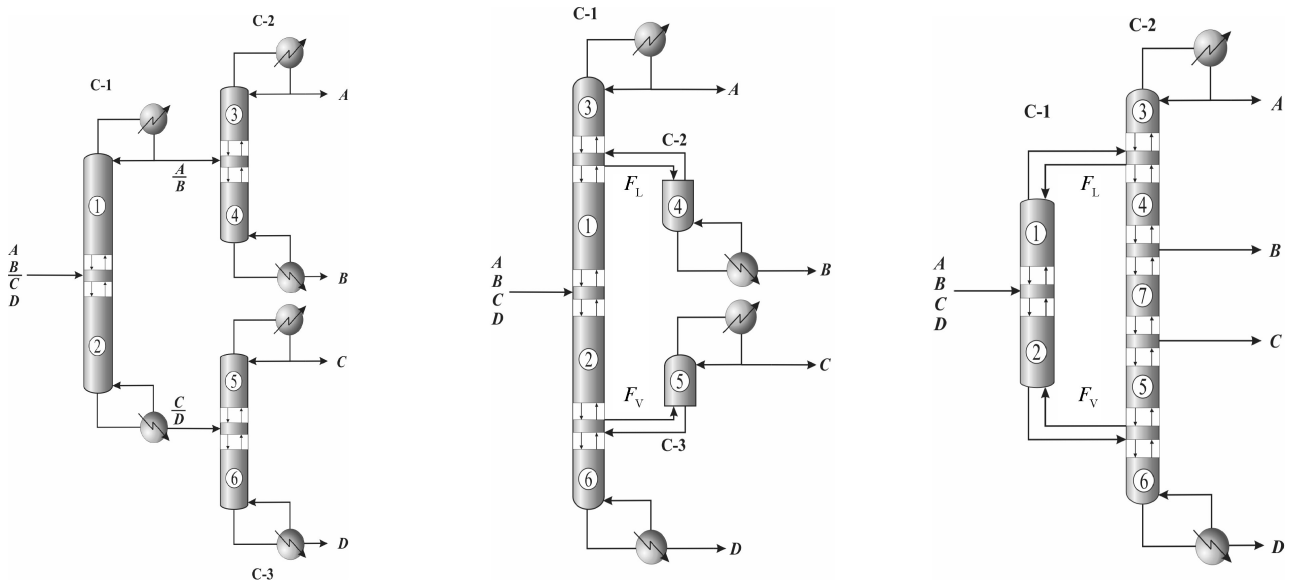


Fig. 4 – Conventional and thermally coupled distillation sequences for the separation of quaternary mixtures: (a) CDS, (b) TCDS-SS/SR, (c) TCDS-PR

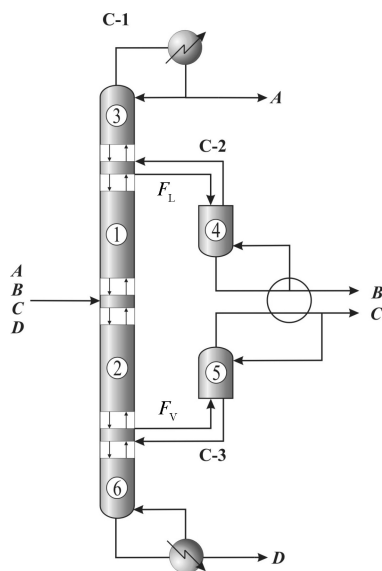


Fig. 5. – Heat-integrated and thermally coupled distillation sequence (TCDS-IN) for the separation of quaternary mixtures

are not trivial because of the recycle stream between the two distillation columns. The optimised designs were obtained in two stages: i) the conventional distillation sequences of Figure 3 were used as initialization for the optimisation, and ii) recycle streams are introduced from the second column to the first column as indicated in Figure 1.

For the TCDS-D (Figure 1a), a vapour recycle stream is taken from the second column and introduced in the bottoms of the first column (removing the reboiler). The recycle stream is varied until the

minimum energy consumption is obtained in the reboiler of the second column. When the TCDS-I (Figure 1b) is considered, the recycle stream is in the liquid phase and is introduced in the top of first column which removes the condenser. Again, the recycle stream is varied until the minimum energy demand in the reboilers is detected. Both thermally coupled distillation sequences require three design specifications in order to guarantee the purities in the products. The detailed design method is reported in *Hernández and Jiménez*.<sup>10</sup>

The designs of the heat-integrated distillation sequences of Figure 2 are obtained from the conventional distillation sequences of Figure 3. It is important to consider that the heat duty from the condenser in the first column is used in the reboiler of the second column (Figure 2a) and pressures are set to obtain at least a difference of 10 °C between the top of the first column and the bottoms of the second column. The heat-integrated distillation sequence of Figure 2b requires that the overhead product of the second column boils the bottoms of the first column. As a result, the second column requires a higher operational pressure than that in the first column.

When quaternary mixtures are considered, the design and optimisation of the thermally coupled distillation sequences of Figures 4b, 4c, and 5, are even more complex because two recycle streams are present. Both recycle streams need to be varied to obtain the design with the minimum requirement of energy. The complete method is reported in *Blancarte-Palacios et al.*<sup>6</sup>

## Second law efficiencies

The optimised designs of the distillation sequences were studied using the first and second law of thermodynamics. The enthalpies and entropies required were obtained from the process simulator Aspen Plus 11.1™. The standard expressions to calculate second law efficiencies were taken from the work of Seader and Henley<sup>9</sup> and are presented here.

Energy balance:

$$\sum_{\text{out of system}} (nH_m + Q + W_s) - \sum_{\text{in to system}} (nH_m + Q + W_s) = 0 \quad (1)$$

Entropy balance:

$$\sum_{\text{out of system}} \left( nS_m + \frac{Q}{T_s} \right) - \sum_{\text{in to system}} \left( nS_m + \frac{Q}{T_s} \right) = \Delta S_{\text{irr}} \quad (2)$$

Exergy balance:

$$\sum_{\text{in to system}} \left[ nE_m + Q \left( 1 - \frac{T_0}{T_s} \right) + W_s \right] - \sum_{\text{out of system}} \left[ nE_m + Q \left( 1 - \frac{T_0}{T_s} \right) + W_s \right] = W_L \quad (3)$$

Minimum work of separation:

$$W_{\text{min}} = \sum_{\text{out of system}} nE_m - \sum_{\text{in to system}} nE_m \quad (4)$$

Second law efficiency:

$$\eta = \frac{W_{\text{min}}}{W_L + W_{\text{min}}} \quad (5)$$

Exergy function:

$$E_m = H_m - T_0 S_m \quad (6)$$

Lost work in the system:

$$W_L = T_0 \Delta S_{\text{irr}} \quad (7)$$

It is important to mention that contributions in the field of exergy analysis have been reported regarding distillation columns. Agrawal and Fidkowski<sup>11</sup> obtained that important savings in total annual costs can be achieved in distillation columns by using intermediate reboilers in the rectifying section and intermediate condensers in the stripping section. Such arrangements let use less expensive utilities in the separation of highly non ideal mixtures. Rivero<sup>12</sup> and Rivero et al.<sup>13</sup> have presented studies of the simulation of diabatic distillation columns (heat exchangers in all stages) and have reported reduction in exergy loss by diabatization of distilla-

tion columns. Koeijer and Rivero<sup>14</sup> have compared the exergy loss in one diabatic experimental distillation column and one adiabatic distillation column. They found that the second law efficiency, in the case of the diabatic distillation column, was increased significantly in contrast to that obtained in the adiabatic distillation column for the separation of a mixture of water/ethanol. Also, the most important conclusion presented was that diabatic distillation columns presented lower exergy loss than adiabatic distillation columns. Jiménez et al.<sup>15</sup> have pointed out the importance of significantly exergy savings by diabatization of distillation columns through the use of heat exchangers in series.

## Case of study

Table 1 contains the mixtures separated using the distillation sequences under investigation. Mixtures M<sub>1</sub> and M<sub>2</sub> were studied for ternary systems of distillation (Figures 1 through 3) and quaternary schemes of distillation (Figures 4 and 5), respectively. The feed composition corresponds to a typical case study used in thermally coupled distillation sequences, i.e., the amounts of the intermediate components are lower than those of the lightest and heaviest components. For the quaternary mixture, molar fractions of the components in the feed stream are 0.3, 0.2, 0.2 and 0.3 for A, B, C and D, respectively. When the ternary mixture is considered, molar fractions of the components are 0.45, 0.1 and 0.45 for A, B and C, respectively.

Table 1 – Mixtures separated in the distillation sequences

Mixture	Components
M <sub>1</sub>	n-pentane, n-hexane, n-heptane
M <sub>2</sub>	n-pentane, n-hexane, n-heptane, n-octane

## Results

### Energy demands in the reboilers

Tables 2 and 3 present the design variables for the energy-efficient designs of the distillation sequences which were obtained by using Aspen Plus 11.1™. Also, a pressure drop of 69 kPa was assumed in each distillation column; this choice allows for the use of cooling water in the condenser of each unit.

Table 4 shows the energy requirements for the separation of mixture M<sub>1</sub>. The results indicate that the thermally coupled distillation sequences (TCDS-D and TCDS-I) can offer energy savings of up to 30 % in contrast to the best conventional dis-

Table 2 – Steady state design variables for ternary separations

sequence	DS		IS		DSI		ISI		TCDS-D		TCDS-I	
	C-1	C-2	C-1	C-2	C-1	C-2	C-1	C-2	C-1	C-2	C-1	C-2
top pressure (kPa)	144.8	101.4	101.4	144.8	888.1	101.4	101.4	888.1	144.8	101.4	101.4	144.8
reflux ratio (Molar)	2.59	3.18	1.06	2.41	2.59	3.18	1.06	2.41	2.96	1.98	0.52	5.55
total stages	17.0	18.0	20.0	17.0	17.0	18.0	20.0	17.0	17.0	18.0	20.0	17.0
reboiler duty (kW)	410.6	481.2	521.0	399.3	410.6	100.9	157.1	399.3	0.0	787.4	555.6	175.1

Table 3 – Steady state design variables for quaternary separations

TCDS-SS/SR	TCDS-IN	TCDS-PR	CDS
<i>Column C-1</i>	<i>Column C-1</i>	<i>Column C-1</i>	<i>Column C-1</i>
Top pressure = 145.35 kPa	Top pressure = 145.35 kPa	Top pressure = 145.35 kPa	Top pressure = 101.35 kPa
Section 1 = 8	Section 1 = 8	Section 1 = 8	Section 1 = 8
Section 2 = 5	Section 2 = 5	Section 2 = 5	Section 2 = 5
Section 3 = 9	Section 3 = 9		Reflux Ratio = 1.2
Section 6 = 8	Section 6 = 8	<i>Column C-2</i>	Reboiler Duty = 325 kW
Reflux Ratio = 8.27	Reflux Ratio = 8.27	Top pressure = 145.35 kPa	
Reboiler Duty = 679.6 kW	Reboiler Duty = 679.6 kW	Section 3 = 9	<i>Column C-2</i>
$F_L = 28.60 \text{ kmol h}^{-1}$	$F_L = 28.60 \text{ kmol h}^{-1}$	Section 4 = 8	Top pressure = 145.35 kPa
$F_V = 56.75 \text{ kmol h}^{-1}$	$F_V = 56.75 \text{ kmol h}^{-1}$	Section 5 = 11	Section 3 = 9
		Section 6 = 8	Section 4 = 8
<i>Column C-2</i>	<i>Column C-2</i>	Section 7 = 12	Reflux Ratio = 2.038
Top pressure = 145.35 kPa	Top pressure = 145.35 kPa	Reflux Ratio = 11.59	Reboiler Duty = 266.6 kW
Section 4 = 8	Section 4 = 8	Reboiler Duty = 851.1 kW	
Reboiler Duty = 93.47 kW		Liquid Side Product = 11.29 kmol h <sup>-1</sup>	<i>Column C-3</i>
	<i>Column C-3</i>	$F_L = 31.78 \text{ kmol h}^{-1}$	Top pressure = 101.35 kPa
<i>Column C-3</i>	Top pressure = 145.35 kPa	$F_V = 54.48 \text{ kmol h}^{-1}$	Section 5 = 11
Top pressure = 145.35 kPa	Section 5 = 11		Section 6 = 8
Section 5 = 11	Reflux Ratio = 1.90		Reflux Ratio = 3.243
Reflux Ratio = 1.90			Reboiler Duty = 388.4 kW

Table 4 – Energy consumptions and second law efficiencies for the distillation sequences

Distillation sequence	Power consumption, kW	Energy saving, %	Second law efficiency, %	Distillation sequence	Power consumption, kW	Energy saving, %	Second law efficiency, %
Mixture M <sub>1</sub>				Mixture M <sub>2</sub>			
TCDS-D	620.0	14.0	21	CDS	966.0	0.0	20
TCDS-I	504.5	30.0	28	TCDS-SS/SR	773.0	20.0	22.5
DSI	416.0	42.0	22.4	TCDS-PR	851.0	12.0	10.5
ISI	419.5	41.8	29.4	TCDS-IN	586.1	39.0	24.2
DS	721.0	0	13				
IS	737.5	-2.2	21				

tillation option (DS). When the heat-integrated distillation schemes (DSI and ISI) are compared to the conventional DS option, energy savings of up to 42 % are found. It is important to mention that, in spite of the lowest energy consumptions achieved in heat-integrated distillation sequences, the utilities required in the reboilers of such systems are more expensive because of their higher operational pressures in comparison to those needed in the conventional distillation sequences.

For the separation of mixture  $M_2$ , the thermally coupled distillation sequences present energy savings between 12 and 20 %. We can see that the introduction of heat integration in the TCDS-SS/SR increased the energy saving up to 39 %. Hence, the energy savings in distillation trains can be increased through the use of, both, thermal links and heat integration between condensers and reboilers.

### Second law efficiencies

The efficiency in the use of the energy is better in the thermally coupled distillation sequences for the case of the separation of mixture  $M_1$ . The indirect distillation sequences (TCDS-I, ISI and IS) present higher second law efficiencies than the direct distillation sequences (TCDS-D, DSI and DS). This can be explained in terms of the temperatures in the reboilers, the indirect distillation sequences require energy in the reboilers at lower temperatures than the direct distillation sequences. As indicated in Table 4, the second law efficiency is increased through the use of thermal links and heat integration because of the reduction in the energy, despite the fact that in the heat-integrated distillation sequences, the energy required in the reboilers is supplied at higher temperatures than those of the conventional distillation sequences.

For the quaternary mixture  $M_2$ , the TCDS-IN presented, both, highest energy savings and second law efficiencies due to two thermal links and heat integration. The thermally coupled distillation sequence with a prefractionator (TCDS-PR) presented the lowest second law efficiency, because all the energy required to distill the quaternary mixture is introduced at the highest temperature in the distillation sequence.

### Conclusions

Energy demands and second law efficiencies to distill ternary and quaternary mixtures of hydrocarbons for conventional, thermally coupled, heat-integrated and, both, thermally and heat-integrated distillation sequences were obtained and compared. When a ternary mixture was analysed, thermally coupled and heat-integrated distillation sequences

presented energy savings up to 30 and 42 %, respectively, in contrast to conventional distillation sequences. Regarding thermodynamic efficiency, in most of the cases the introduction of thermal links increased its value, but this increment was not superior to 9 %; such an increment is caused by the reduction in energy consumption through the use of thermal links. For the heat-integrated distillation sequences, despite the fact that the energy consumptions were reduced significantly, the increment in the second law efficiency was similar to that of the thermally coupled distillation sequences because of the use of energy at higher temperature.

For a quaternary mixture of hydrocarbons, again important energy savings were observed in the thermally coupled distillation sequences and the introduction of heat integration increased the energy savings. When the thermally coupled distillation sequence with a prefractionator was analysed, its thermodynamic efficiency was lower than that obtained in the conventional distillation sequence, because all the energy required to distill the quaternary mixture is supplied at the highest level of temperature. It was obtained that the thermal links and heat integration increase, both, energy savings and the second law efficiency.

### ACKNOWLEDGEMENTS

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### Nomenclature

ABC	– ternary mixture
ABCD	– quaternary mixture
$C_1$	– first column
$C_2$	– second column
$C_3$	– third column
$E_m$	– molar energy, $\text{kJ mol}^{-1}$
$H_m$	– molar enthalpy, $\text{kJ kmol}^{-1}$
$F_L$	– interconnecting liquid flow rate, $\text{kmol h}^{-1}$
$F$	– molar flow rate, $\text{kmol h}^{-1}$
$n$	– amount of substance, kmol
$Q$	– heat, kJ
$S_m$	– molar entropy, $\text{kJ kmol}^{-1} \text{K}^{-1}$
$T_0$	– temperature of the surroundings, K
$T_s$	– temperature of the system, K
$F_V$	– interconnecting vapour flow, $\text{kmol h}^{-1}$
$W_{\min}$	– minimum work for the separation, kW
$W_s$	– shaft work, kW
$\Delta S_{\text{irr}}$	– production of entropy due to the irreversibility, $\text{kJ K}^{-1}$
$\eta$	– second law efficiency

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