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Energy, exergy, and Second Law performance criteria

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Abstract

Performance criteria, such as efficiencies and coefficients of performance, for energy systems, are commonly used but often without sufficient understanding and consistence. The situation becomes particularly incoherent when simultaneous energy interactions of different types, such as work, heating and cooling, take place with a system. Also, the distinction between exergy and Second Law efficiencies is not clearly recognized by many. It is attempted here to clarify the definitions and use of energy and exergy based performance criteria, and of the Second Law efficiency, with an aim at the advancement of international standardization of these important concepts.

Keywords: Thermodynamics; Efficiency; Exergy; Second Law; Performance

1. Introduction

There are many ways to assess energy system performance, and they must be adapted to the particular use they are put to. While the underlying concepts of such assessments are often well known and documented for a number of systems and cases, there are no clear agreements or rules about efficiency definitions, and authors often use different, and sometimes unsuitable, efficiency definitions for the same systems. The situation becomes particularly incoherent when simultaneous energy interactions of different types, such as work, heating and cooling, take place with a system. This prevents logical comparison of results at best, and wrong results at worst. This paper is intended to provide some clarifications and uniformity in that area, make a few proposals, and start a discussion that would hopefully lead to accelerated international standardization of these important concepts.

The most common energy system performance assessment criteria are *energy based* (“first law”) and they are useful for assessing the efficiency of energy use, and can be easily converted to energy cost efficiencies if the prices of the energy forms of the useful outputs and paid inputs are known. Here we define as “useful” all energy interactions that have been used by the system “owner”, usually in terms of monetary value, and “paid” all energy interactions that have a direct cost, usually monetary, to the system owner. Thus, for example, the heat inputs that come from the environment for which the owner does not need to pay are not included. We hasten to add that analyses that address environmental impact will include exchanges with the environment too.

Since such energy-based criteria do not account for the quality of energy, expressed as exergy, *exergy-based* criteria are also appropriate as they account better for use of energy resources and give much better guidance for system improvement. They also can be converted to exergy cost efficiencies if the exergy values of the useful outputs and paid inputs can be rationally priced.

Another set of criteria assess the difference between the performance of a system relative to an ideal one (reversible) that operates between the same thermodynamic limits. We shall call these *Second Law-based* criteria, although many authors use this term for exergy-based criteria.

Ultimately, decisions on best designs are most often based on economical considerations, in which energy (or

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Nomenclature

a	specific exergy, J/kg; price of energy unit, \$/MJ
A	exergy, J
b	price of exergy unit, \$/MJ
c_p	specific heat at constant pressure, J/kg k
c_v	specific heat at constant volume, J/kg k
COP	coefficient of performance
$C\tilde{O}P$	reversible cycle coefficient of performance, Eq. (105)
E	energy, J
h	specific enthalpy, kJ/kg
I	irreversibility, J
j	the number of useful work or inputs and outputs
ke	specific kinetic energy, J/kg
$\dot{m}$	mass flow rate of a stream
n	the number of paid-for heat inputs
q	heat per unit mass, J/kg
pe	specific potential energy, J/kg
P	pressure, Pa
Q	heat, J
$\overset{\frown}{Q}$	heat invested in plant construction, J
r_c	the useful cooling to work output ratio, Eq. (89)
r_h	the useful heat to work output ratio, Eq. (90)
R	universal gas constant
$R_{\mathrm{I},e}$	First Law environmental impact ratio, Eq. (13)
s	specific entropy, J/kg k
S	entropy, J/K
S_{gen}	entropy generation, J/K
t	time, s
T	temperature, K
$\hat{T}$	entropic temperature, Eq. (54), K
v	specific volume, m^3
w	specific work, J/kg
W	work, J
$\hat{W}$	work invested in plant construction, J
x	price per unit exergy of heat, \$/MJ

Greek letters

ε	exergy efficiency
$\hat{\varepsilon}_t$	The "total" (or "overall") unsteady state exergy efficiency
$\tilde{\varepsilon}_t$	The "total" (or "overall") steady state exergy efficiency, including the system exergy
η_{I}	energy (First Law) efficiency
$\eta_{\mathrm{I}em}$	embodied energy efficiency
$\eta_{\mathrm{I}u}$	utilitarian (task) energy efficiency
$\eta_{\mathrm{I}\$}$	economic energy efficiency
η_{II}	Second Law efficiency
η_Q	useful heat production efficiency in a cogeneration cycle, Eq. (92)
η_w	work production efficiency in a cogeneration cycle, Eq. (91)
$\hat{\eta}_{\mathrm{I}}$	energy efficiency when the total energy content of the system is taken into consideration
$\tilde{\eta}_{hp}$	heat input based reversible cycle efficiency definition, Eq. (104)
$\tilde{\eta}_{hu}$	heat output based reversible cycle efficiency definition, Eq. (106)
$\tau_{payback}$	energy payback time, years

Subscripts

0	dead state
a	absorber
c	cooling, or cold temperature reservoir
con	condenser
cu	for refrigeration use
cp	paid-for refrigeration
d	direct
e	environment of a system
em	embodied, Eq. (12)
E	direct energy invested in plant construction
f	heating or cooling fluid
h	heating, or high temperature reservoir
hp	paid-for heat
hu	for heating use
i	incoming
I	First Law
II	Second Law
j	index, the jth heat or work exchange
k	number of material products of a plant
l	labor
L	index of energy needed for restoration of the environment to its original state
m	materials
o	outgoing
p	paid for
rev	reversible
s	system
t	total
u	useful

exergy) are only one part, and sometimes not the most significant one, where the other parts include capital investment, labor, insurance, taxes, etc.

It is also worth noting that while performance criteria are most often applied to the entire system, such as plant or energy conversion device, they can be applied at any level, such as to different components, inside spatial and temporal processes, and down to the smallest particle interactions, when there is an interest in that kind of exploration.

2. Energy-based criteria

2.1. Introduction

There are many definitions of energy efficiency, based on need (or greed…), and some of the more common ones are reviewed below.

2.2. Total energy efficiency

We start with the energy conservation equation for a system (Fig. 1) undergoing a process from state 1 to state 2, where the values of the system energy at these states are E_1 and E_2, respectively, and which undergoes j work and heat interactions

$$\begin{aligned} E_1 - E_2 &= \sum_j W_{o,j} + \sum_j Q_{o,j} - \left(\sum_j Q_{i,j} + \sum_j W_{i,j}\right) \\ &= W_o + \left(Q_{o,h} - Q_{o,c} + Q_{o,e}\right) \\ &\quad - \left[W_i + \left(Q_{i,h} - Q_{i,c} + Q_{i,e}\right)\right], \end{aligned} \tag{1}$$

where in the second line we use the notation

$$\begin{aligned} &W_o \equiv \sum_j W_{o,j} \quad W_i \equiv \sum_j W_{i,j}, \\ &Q_{o,h} - Q_{o,c} + Q_{o,e} \equiv \sum_j Q_{o,j}, \\ &Q_{i,h} - Q_{i,c} + Q_{i,e} \equiv \sum_j Q_{i,j} \end{aligned} \tag{2}$$

for compactness; the terms Q express the thermal energy interactions of heating, cooling, and heat interactions with the environment.

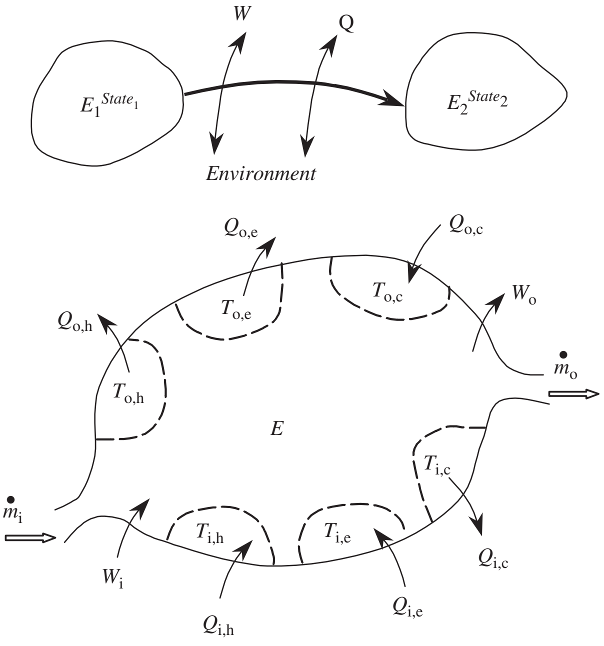


Fig. 1. Energy interactions.

As usual, both the work and heat terms may be composed of flow and direct components, or in general

$$W = \dot{m}(ke + pe) + W_d, \quad Q = \dot{m}h + Q_d, \tag{3}$$

where $\dot{m}$ is the mass flow rate of the stream carrying the specific kinetic and potential energy work, or h in or out of the system, and W_d *and* Q_d are the direct energy input to- and output from- the system. For work terms the latter may be a direct mechanical interaction with the system, such as a stirrer inserted into it, and for heat ones it may be irradiation or any exothermic reaction.

A *total* energy efficiency $\hat{\eta}_{\mathrm{I}t}$ can be defined in its broadest manner as

$$\begin{aligned} \hat{\eta}_{\mathrm{I}t} &= \frac{E_2 + \sum_j W_{o,j} + \sum_j Q_{o,j}}{E_1 + \sum_j Q_{i,j} + \sum_j W_{i,j}} \\ &= \frac{E_2 + W_o + \left(Q_{o,h} - Q_{o,c} + Q_{o,e}\right)}{E_1 + W_i + \left(Q_{i,h} - Q_{i,c} + Q_{i,e}\right)} = 1. \end{aligned} \tag{4}$$

Obviously, the ratio of all energy outputs to inputs, Eq. (4), is always equal to 1 and is thus useless for system performance assessment, although it should always be used in computations as a part of results validation.

Most often, the steady-state total energy efficiency is defined without consideration of the energy value of the system, E, to more clearly focus on the energy inputs and outputs only, and thus the best known form of the steady-state total energy efficiency takes the form

$$\eta_{\mathrm{I}t} \equiv \frac{\sum_j W_{o,j} + \sum_j Q_{o,j}}{\sum_j Q_{i,j} + \sum_j W_{i,j}} = \frac{W_o + \left(Q_{o,h} - Q_{o,c} + Q_{o,e}\right)}{W_i + \left(Q_{i,h} - Q_{i,c} + Q_{i,e}\right)} = 1. \tag{5}$$

2.3. Common energy efficiencies

There are variants of the total energy efficiency that selectively include some of the inputs and/or outputs to analyze some particular aspect of energy use, and examples are shown below.

2.3.1. The common energy efficiency $\eta_{\mathrm{I}u}$

The common (utilitarian, or "task") energy (First Law) efficiency $\eta_{\mathrm{I}u}$ is based on the practical energy needs (work, heat, refrigeration) of the system owner that are satisfied by the system, divided by the energy inputs to the system that must be "paid" for. The practical extension of this thermodynamic definition is to define the numerator terms as having a monetary benefit value, and those in the denominator as having a monetary cost, to the system owner. For a general system with *used* work, heat and refrigeration outputs, and *paid* work, heat and refrigeration inputs (a preliminary discussion of such combined system efficiencies can be found in [1,2]), it is in general usually best expressed in terms of their absolute values as

$$\eta_{\mathrm{I}u} = \frac{\sum_j \left|W_{u,j}\right| - \sum_j \left|W_{p,j}\right| + \sum_j \left|Q_{hu,j}\right| + \sum_j \left|Q_{cu,j}\right|}{\sum_j \left|Q_{hp,j}\right| + \sum_j \left|Q_{cp,j}\right|}, \tag{6}$$

noting that in this case it is assumed that positive net power is produced for use, $\sum_j |W_{u,j}| > \sum_j |W_{p,j}|$, and thus the paid work inputs (consumption) $\sum_j |W_{p,j}|$ are subtracted from the useful work outputs $\sum_j |W_{u,j}|$ in the numerator of Eq. (6) rather than added to the denominator. This is an important distinction, because the latter definition is more consistent with thermodynamic logic but gives higher values of η_{1u} that favor the system vendor (see Appendix A for the somewhat trivial proof).

If $\sum_j |W_{u,j}| < \sum_j |W_{p,j}|$, the definition of $\eta_{\mathrm{I}u}$ that is consistent with Eq. (6), favoring the customer, is

$$\eta_{\mathrm{I}u} = \frac{\sum_j |Q_{hu,j}| + \sum_j |Q_{cu,j}|}{\sum_j |Q_{hp,j}| + \sum_j |Q_{cp,j}| + \sum_j |W_{p,j}| - \sum_j |W_{u,j}|}. \tag{7}$$

2.3.2. *The coefficient of performance, COP*

This terminology is used mostly in evaluating the performance of systems that produce primarily cooling, and the definition is actually identical to that of $\eta_{\mathrm{I}u}$, Eq. (7). When the only product is cooling, and no cooling inputs to the system are present, Eq. (7) is reduced to

$$\eta_{\mathrm{I}u} = \frac{\sum_j |Q_{cu,j}|}{\sum_j |Q_{hp,j}| + \sum_j |W_{p,j}| - \sum_j |W_{u,j}|} = COP, \tag{8}$$

which is commonly used to characterize cooling systems that have both heat and work inputs, such absorption ones. For cooling systems that do not use heat inputs, Eq. (8) is reduced to

$$COP = \frac{\sum_j |Q_{cu,j}|}{\sum_j |W_{p,j}| - \sum_j |W_{u,j}|}. \tag{9}$$

In fact, few cooling systems produce useful work and then the term $\sum_j |W_{u,j}|$ in Eqs. (8) and (9) is zero.

2.4. *Embodied energy efficiency*

It is often of interest (or should be…) to include in the energy efficiency assessment also the energy embodied in the production of the plant, in the materials produced by it, and in the materials and labor needed for its operation and for the distribution of its material products to the customer. Such a criterion answers, for example, the commonly posed question on the length of time that it takes for an energy conversion system to generate the energy originally required for its manufacturing and operation. For example, Table 1 shows the numbers of years of successful operation that it takes to pay back the energy invested in the construction of several types of energy conversion systems.

Table 1
Energy payback for some power generation systems

Type of system	Energy payback, years	Reference
Coal power plant	3.6	[3]
Nuclear power plant	2.6	[3]
Solar domestic hot water system	1.3–2.3	[4,5]
Solar photovoltaic system	2–6	[5,6]
Wind-electric generator	0.25–0.67	[7]

The equation commonly used for that energy payback period $\tau_{payback}$, in years, is

$$\tau_{payback} = \frac{\left(\sum_j |\hat{W}_j| + \sum_j |\hat{Q}_{h,j}| + \sum_j |\hat{Q}_{c,j}|\right)_{E,m,l}}{\left(\sum_j |W_{u,j}| - \sum_j |W_{p,j}| + \sum_j |Q_{hu,j}| + \sum_j |Q_{cu,j}|\right)_{peryear}}, \tag{10}$$

where the numerator is the total energy (the terms marked by the overbar ˆ) invested in the direct energy demand (subscript *E*), and energy content of the materials (*m*), and labor (*l*) needed for the system construction, and the denominator is the annual production of useful energy (net work, heat, refrigeration).

In fact, a more consistent definition of $\tau_{payback}$ would also include in the numerator of Eq. (10) the total energy investment, embodied in the fuel, materials and labor needed for the plant operation over its lifetime (*L* years), and would also included in the denominator the energy embodied in non-energy *k* products of the plant, $\left(\sum_k |E_k|\right)_m$.

To create a more equitable comparison between systems that produce different impacts on the environment, these embodied energies should also include the energy needed for restoration of the environment to its original state (the second term in the numerator, index *L*). With the annual embodied heating and cooling investments (the second term in the numerator), the equation would then become

$$\tau_{payback,t} = \frac{\left[\left(\sum_j |\hat{W}_j| + \sum_j |\hat{Q}_{h,j}| + \sum_j |\hat{Q}_{c,j}|\right)_{E,m,l} + \sum_1^L \left(\sum_j |Q_{hp,j}| + \sum_j |Q_{cp,j}|\right)_{E,m.l}\right]}{\left[\sum_j |W_{u,j}| - \sum_j |W_{p,j}| + \sum_j |Q_{hu,j}| + \sum_j |Q_{cu,j}| + \left(\sum_k |E_k|\right)_m\right]_{peryear}}. \tag{11}$$

In energy efficiency form, such a more comprehensive expression would be an extension of Eq. (6), which adds the annualized investment in the construction of the plant and in the materials and labor needed in its regular operation

$$\eta_{\mathrm{I},em} = \frac{\left[\sum_j |W_{u,j}| - \sum_j |W_{p,j}| + \sum_j |Q_{hu,j}| + \sum_j |Q_{cu,j}| + \left(\sum_k |E_k|\right)_m\right]}{\left[\left(\sum_j |W_j| + \sum_j |Q_{h,j}| + \sum_j |Q_{c,j}|\right)_{E,m,l} + \left(\sum_j |Q_{hp,j}| + \sum_j |Q_{cp,j}|\right)_{E,m,l}\right]}, \tag{12}$$

where the last term in the numerator, $\left(\sum_k |E_k|\right)_m$, denotes the embodied energy in the *k* types of materials produced by the plant, and the first (bracketed) term in the denominator is composed of the annualized energy investment in the production of the plant, and the second term is the annual embodied energy invested in the energy sources, materials and labor needed for its regular operation. All the energy terms are rates.

2.5. Energy criteria considering environmental effects

In some circumstances the objective of the analysis may include the energy impact of the system on the environment, including heat rejection to the environment or heat absorption from it, even though no direct (or immediate) monetary cost or benefit may be associated with it. This also would be of interest for finding the effects on ambient cooling or heating water consumption, etc. In that case we can define a thermal environmental impact ratio, $R_{\mathrm{I},e}$, all of the heat interactions with the environment (heat rejection and absorption) to the sum of the useful net power, heating and cooling produced, as

$$R_{\mathrm{I},e} = \frac{\sum_i Q_{e,i}}{\sum_i \left|W_{u,i}\right| - \sum_i \left|W_{p,i}\right| + \sum_i \left|Q_{hu,i}\right| + \sum_i \left|Q_{cu,i}\right|}. \tag{13}$$

2.6. Evaluation criteria based on economics

The focus of this paper is on the technical aspects of energy conversion system performance criteria, but for completeness it is noted that decisions on industrial/commercial systems are typically based on economic considerations. As stated in the Introduction, the energy performance, as characterized by the different performance criteria described above, is only one of the components of the total cost. Typical energy performance criteria include payback period, return on investment (ROI), and life cycle cost analysis (cf. [8]), and those can be either restricted to the direct energy streams, or to the energy streams included embodied energy, for example as in Eq. (12). Nevertheless, we can, for some specific purposes, define a First Law economics efficiency, $\eta_{\mathrm{I}\$}$, by including the prices of the different heat and work inputs and outputs, and Eq. (6) becomes

$$\eta_{\mathrm{I}\$} = \frac{\left[\sum_j b_{u,j}\left|W_{u,j}\right| - \sum_j b_{p,j}\left|W_{p,j}\right| + \sum_j a_{hu,j}\left|Q_{hu,j}\right| + \sum_j a_{cu,j}\left|Q_{cu,j}\right|\right]}{\sum_j a_{hp,j}\left|Q_{hp,j}\right| + \sum_j a_{cp,j}\left|Q_{cp,j}\right|} \tag{14}$$

and Eq. (7) becomes

$$\eta_{\mathrm{I}\$} = \frac{\sum_j a_{hu,j}\left|Q_{hu,j}\right| + \sum_j a_{cu,j}\left|Q_{cu,j}\right|}{\left[\sum_j a_{hp,j}\left|Q_{hp,j}\right| + \sum_j a_{cp,j}\left|Q_{cp,j}\right| + \sum_j b_{p,j}\left|W_{p,j}\right| - \sum_j b_{u,j}\left|W_{u,j}\right|\right]}, \tag{15}$$

where the coefficients a and b are the specific prices of the different types of heat and work, respectively, say in \$/MJ . Eqs. (14) and (15) express how much money is gained from the useful heat and work products per monetary unit invested in the paid heat and power consumed by the system.

3. Exergy efficiency, ε

3.1. Introduction

Just as there are various definitions of energy efficiencies as discussed above, there are also various definitions of exergy efficiency. Sorting out the different definitions to avoid misunderstandings and contribute to uniformity has been the subject of a number of papers from Germany in the 1950s and 1960s (cf. [9–14]). We discuss here overall efficiency, the utilitarian (or "task") efficiency, and some ways to define the exergy.

Of help in these definitions is the exergy accounting of the system. For a thermodynamic system going through interactions between an initial state 1 and a later state 2, where the system exergy values are $A_{s,1}$ and $A_{s,2}$, respectively, the equation representing this accounting is

$$A_{s,2} - A_{s,1} = \sum\nolimits_i A_i - \sum\nolimits_o A_o - I, \tag{16}$$

where A_i and A_o are the exergy inputs and outputs to and from the system, respectively, and I is the total exergy loss (or destruction). Due to the Second Law, $I \geqslant 0$.

In steady state $A_{s,1} = A_{s,2}$, and Eq. (16) gives

$$\sum\nolimits_o A_o = \sum\nolimits_i A_i - I. \tag{17}$$

The irreversibility I is linked to the entropy generation S_{gen} by the equation

$$I = T_0 S_{gen}, \tag{18}$$

where T_0 is the dead state temperature (in absolute units).

3.2. The "total" (or "overall") exergy efficiency, $\hat{\varepsilon}_t$

$$\hat{\varepsilon}_t \equiv \frac{\left[(\text{the system exergy at state 2}) + \left(\sum_o \text{all exergy outputs}\right)\right]}{\left[(\text{the system exergy at state 1}) + \left(\sum_i \text{all exergy inputs}\right)\right]} = \frac{A_{s,2} + \sum_o A_o}{A_{s,1} + \sum_i A_i} \tag{19}$$

and, as before, the ingoing and outgoing exergy quantities may include work, heat and cooling, with or without mass flows. Incorporating Eq. (16) into (19) gives

$$\hat{\varepsilon}_t = \frac{A_{s,1} + \sum_i A_i - I}{A_{s,1} + \sum_i A_i} = 1 - \frac{I}{A_{s,1} + \sum_i A_i}. \tag{20}$$

This also shows that $\hat{\varepsilon}_t \leqslant 1$, where the equality applies to completely reversible processes. This is unlike the overall energy efficiency η_{I_t} [Eqs. (4) and (5)] which is always equal to unity, because energy is conserved, while exergy always decreases in all real (irreversible) processes.

$\hat{\varepsilon}_t$ is used when the overall exergy efficiency of a system needs to be calculated, without interest in some of the individual outputs of the system. It is especially applicable when the system input and output streams do not maintain their integrity and the major part of the output is useful. It also has a more thermodynamic flavor than other efficiency definitions, in that it evaluates the efficiency of a process giving equal consideration to all outputs and inputs regardless of whether they are being used or paid for. For example, it offers a good starting point for ecological analysis of processes since it takes into equal consideration exergy components as diverse as useful work, heat and product materials on the one hand, and material and heat emissions to the environment on the other, on the output side, and paid fuel, work, and materials on the one hand, and "free" environmental heat on the other, on the input side.

In steady state $A_{s,1} = A_{s,2} = A_s$ and Eqs. (19) and (20) become

$$\tilde{\varepsilon}_t \equiv \frac{1 + \left(\sum_o A_o / A_s\right)}{1 + \left(\sum_i A_i / A_s\right)} \tag{21}$$

and

$$\tilde{\varepsilon}_t = 1 - \frac{I}{A_s + \sum_i A_i}, \tag{22}$$

respectively.

Most often, the steady-state total exergy efficiency is defined without consideration of the exergy value of the system, A_s, to more clearly focus on the exergy inputs and outputs only, and thus the best known form of the steady-state total exergy takes the form

$$\varepsilon_t \equiv \frac{\sum_o A_o}{\sum_i A_i} = 1 - \frac{I}{\sum_i A_i}. \tag{23}$$

3.3. The task (or "utilitarian") exergy efficiency, ε_u

Using the same logic as in definition of η_{I}, ε_u can be defined as the ratio between the exergy outputs useful to the owner, and the exergy inputs paid by the owner. The most common is the steady-state definition, and thus the equivalent of Eqs. (6), (7), (14), and (15) are Eqs. (24) and (25) below:

$$\varepsilon_u = \frac{\sum_j |W_{u,j}| - \sum_j |W_{p,j}| + \sum_j |A_{hu,j}| + \sum_j |A_{cu,j}|}{\sum_j |A_{hp,j}| + \sum_j |A_{cp,j}|}, \tag{24}$$

$$\varepsilon_u = \frac{\sum_j |A_{hu,j}| + \sum_j |A_{cu,j}|}{\sum_j |A_{hp,j}| + \sum_j |A_{cp,j}| + \sum_j |W_{p,j}| - \sum_j |W_{u,j}|}, \tag{25}$$

$$\varepsilon_\$ = \frac{\left[\sum_j b_{u,j} |W_{u,j}| - \sum_j b_{p,j} |W_{p,j}| + \sum_j x_{hu,j} |A_{hu,j}| + \sum_j x_{cu,j} |A_{cu,j}|\right]}{\sum_j x_{hp,j} |A_{hp,j}| + \sum_j x_{cp,j} |A_{cp,j}|}, \tag{26}$$

$$\varepsilon_\$ = \frac{\sum_j x_{hu,j} |A_{hu,j}| + \sum_j x_{cu,j} |A_{cu,j}|}{\left[\sum_j x_{hp,j} |A_{hp,j}| + \sum_j x_{cp,j} |A_{cp,j}| + \sum_j b_{p,j} |W_{p,j}| - \sum_j b_{u,j} |W_{u,j}|\right]}, \tag{27}$$

where the coefficients x and b are the specific exergy value prices of the different types of heat and work, respectively, say In \$/MJ. Eqs. (26) and (27) express on an exergy basis how much money is gained from the useful heat and work products per monetary unit invested in the paid heat and power consumed by the system.

3.4. Exergy definitions

As opposed to energy-based performance criteria, where the definitions of the energy interactions with the system are fairly straightforward, it is not so for exergy. To start, any work (including electrical energy) interactions are still straightforward, because they are pure exergy and thus the exergy values of such interactions are equal to their energy values. Non-work energy interactions (heat for example) have values of exergy that depend on both the type of the energy interaction and the definition of the control system under consideration. The latter depends on the objective of the performance analysis. We can classify the types of non-work energy interactions and of typical objectives as follows.

3.4.1. Straight heat input or output

In general, the exergy of the system heat interactions of a system at constant temperature T with an environment at the dead state temperature T_0 is calculated from

$$A_{h,i} = Q_{h,i}(1 - \frac{T_0}{T}), \tag{28}$$

when $T > T_0$ and $Q_{h,i}$ is the heat output from the system to the environment (or to a heat load at T_0), and

$$A_{c,i} = Q_{c,i}(\frac{T_0}{T} - 1), \tag{29}$$

when $T < T_0$ and $Q_{c,i}$ is the heat input from the cooling load at T to the system. So in these cases the task exergy efficiency for a system with just heat input ("paid", $Q_{hp,i}$) at temperature T and work output (used, W_u) is defined as

$$\varepsilon_u = \frac{W_u}{Q_{hp,i}[1 - (T_0/T)]} \tag{30}$$

and for a system with just work input ("paid", W_p) and refrigeration heat input at temperature T (used, $Q_{cu,i}$)

$$\varepsilon_u = \frac{Q_{cu,i}[(T_0/T) - 1]}{W_p}. \tag{31}$$

Eqs. (28) and (29) are often used in defining the exergy value of heat, but it should be clarified that neither of these temperatures, nor the heat quantities, are necessarily constant during the process in the system under consideration. The heat sources may be of variable temperature, and the heat input rate and even the dead state may vary during the process also. In that case, the more general expression of Eq. (28) for example, for a process starting at time t_1 and ending at time t_2 would be

$$\hat{A}_{h,i} = \int_{t_1}^{t_2} Q_{h,i}(1 - \frac{T_0}{T})\,\mathrm{d}t, \tag{32}$$

where all the parameters in the integral may vary with time. For the efficiency, Eq. (30) becomes

$$\hat{\varepsilon}_u = \int_{t_1}^{t_2} \frac{W_u}{Q_{hp,i}(1-(T_0/T))}\,\mathrm{d}t. \tag{33}$$

Similar integrations would also be used in Eqs. (29)–(31) for the refrigeration system when the integrand varies with time.

3.4.2. *Stream-carried exergy*

Exergy can be carried in and out of systems with a mass flow stream at the rate $\dot{m}a$, where $\dot{m}$ is the mass flow rate and a is the specific exergy. a should include all the relevant exergy components including kinetic, potential, thermal, strain, and chemical as explained in detail in [9]. The sketch in Table 2 shows two common flow configurations: (a) in column 2 depicts a case in which the stream does not mix with the system and maintains its integrity, and (b) in column 3 depicts a case where a stream enters the systems, loses its integrity in it, and another stream exits the system.

From a strict thermodynamic perspective of exergy analysis, the exergy inputs should be calculated using Eqs. (34) and (35) given in Table 2, but it is noteworthy that in some cases it may be decided that either the inflow or outflow exergy streams have no value for the purposes of the analysis. In these cases it is assumed that a_1 and/or a_2 are equal to zero. For example, this would be the case when a stream of fluid is used to supply heat to a system and exits the system at conditions which are deemed, often for economical reasons, unusable for further energy extraction. Another example would be when a stream is cooled by the system to a temperature much lower than its entrance one, so that the outlet exergy of the stream is much lower than its entrance one, and thus the outlet exergy may be considered negligible.

The configurations described in Table 2 ignore exergy losses during the exchange between the stream and the system, in other words it is implicitly assumed that these losses are either negligible (infinite exchange coefficients) or that the analysis is not aimed at this purpose. A more rigorous model, which includes the exchange exergy losses, is described in Table 3. (a) in column 2 describes a system where the external stream $1e \rightarrow 2e$ and a system stream $1s \rightarrow 2s$ are interacting while maintaining their integrities. A sample case is when stream $1s \rightarrow 2s$ is the evaporator in a refrigeration system, and stream $1e \rightarrow 2e$ is the fluid that is being cooled by the evaporator (refrigerator).

Eq. (36) in Table 3 represents the exergy balance in this case, where $I_{e\leftrightarrow s}$ is the irreversibility due to the interaction between the streams, and allows the inclusion of this irreversibility in the system efficiency calculation by ascribing the exergy (input or output) value to the external, rather than the system, stream, as was done in the model (a) of Table 2, column 2.

Table 2
External stream-carried exergy configurations and magnitudes

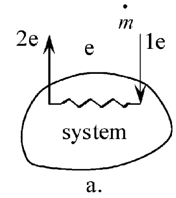
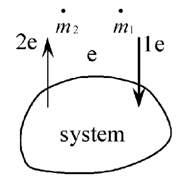
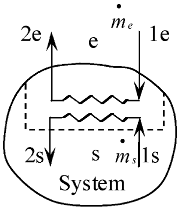
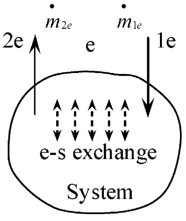
The exergy exchange configuration	 a.	 b.
The exergy change, A	$\dot{m}(a_1 - a_2)$ (34)	$\dot{m}_1 a_1 - \dot{m}_2 a_2$ (35)

Table 3
External stream-carried exergy configurations and magnitudes

The exergy exchange configuration	 a.	 b.
The exergy change, A	$\dot{m}_e(a_{1e} - a_{2e}) = \dot{m}_s(a_{2s} - a_{1s}) + I_{e\leftrightarrow s}$ (36)	$\dot{m}_{1e}\, a_{1e} - \dot{m}_{2e}\, a_{2e} = A_{2s} - A_{1s} + I_{e\leftrightarrow s}$ (37)

Similar to the model (b) of Table 2, column 3, that of the model (b) of Table 3, column 3 represents input and output streams that are not directly connected, but the one (b) in column 3 of Table 3 includes the interactions between these streams and the system, with the associated irreversibility in Eq. (37) of Table 3. A sample case is a combustor with inputs of fuel and oxidant, and an output of reaction products, when the exergy losses due to the combustion process (including mixing, chemical reaction, heat transfer) are wished to be taken into account (cf. [15]). Use of such a model is the basis for "intrinsic" exergy analysis that allows detailed (even spatial and temporal) determination of exergy changes in all interaction processes (cf. [15–18]).

4. Second Law efficiency

4.1. *Introduction*

Given the objectives of the system under consideration, such as power production, cooling, heating, materials processing, etc., and the thermodynamic parameter limits, such as the top and bottom temperatures, pressures, and other thermodynamic potentials, it is useful to compare the performance of the system with one that would deliver the best thermodynamic performance between the same limits, i.e. one in which all the processes are reversible. This indicates clearly a potential for improvement.

The Second Law efficiency is defined here ([2] and many others) as the ratio of the First Law efficiency of the system to the efficiency of a reversible system operating between the same thermodynamic states,

$$\eta_{\mathrm{II}} = \frac{\eta_{\mathrm{I}}}{\eta_{rev}} \tag{38}$$

It is noteworthy that the thermodynamic states must be clearly and correctly defined, especially in view of some practices entrenched in engineering thermodynamics that may be misleading. A good and simple example for such practices (but not of a power cycle) is the concept of the isentropic efficiency of a prime mover. Let us assume (Fig. 2) that steam at pressure P_1 and temperature T_1 is allowed to expand through a turbine to a new lower pressure P_2. If the expansion was reversible and adiabatic, i.e. isentropic, it would proceed to the lowest possible temperature on the lower limit isobar P_2, which we call T_{2s}. Due to the fact that the expansion through the turbine is always irreversible, i.e. some of the available work is converted to heat, the steam, which is still expanding to the isobar P_2, will end at a temperature $T_2 > T_{2s}$.

In common thermodynamic engineering analysis, an "isentropic efficiency" of the turbine is defined as

$$\eta_{isentropic} = \frac{\begin{pmatrix}\text{the work produced by the turbine in the}\\ \text{actual process 1-2, with final state } P_2, T_2\end{pmatrix}}{\begin{pmatrix}\text{the work that would have been produced by the turbine}\\ \text{if the expansion was isentropic, with final state } P_{2s}, T_{2s}\end{pmatrix}} = \frac{h_1 - h_2}{h_1 - h_{2s}}. \tag{39}$$

The performance of the turbine operating between state 1 (P_1, T_1) and state 2 (P_2, T_2) is compared with that which operates isentropically ("ideally") between state 1 (P_1, T_1) and state 2*s* (P_{2s} T_{1s}) that is on the same isobar as state 2 but has the same entropy as state 1. The premise of this definition differs from the definition of the Second Law efficiency in a very important way: the end states for the real and reversible processes in this definition, Eq. (39), are different, while for the definition of the Second Law efficiency in Eq. (38) the end states for the real and reversible processes are the same. Eq. (38)-based definition of the turbine isentropic efficiency would be

$$\eta_{isentropic} = \frac{\begin{pmatrix}\text{the work produced by the turbine in the}\\ \text{actual process 1-2, with final state } P_2, T_2\end{pmatrix}}{\begin{pmatrix}\text{the work that would have been produced by the turbine}\\ \text{if the expansion was reversible, with final state } P_2, T_2\end{pmatrix}} = \frac{W_{1\to 2}}{W_{rev,\,1\to 2}} = \frac{h_1 - h_2}{W_{rev,\,1\to 2}}. \tag{40}$$

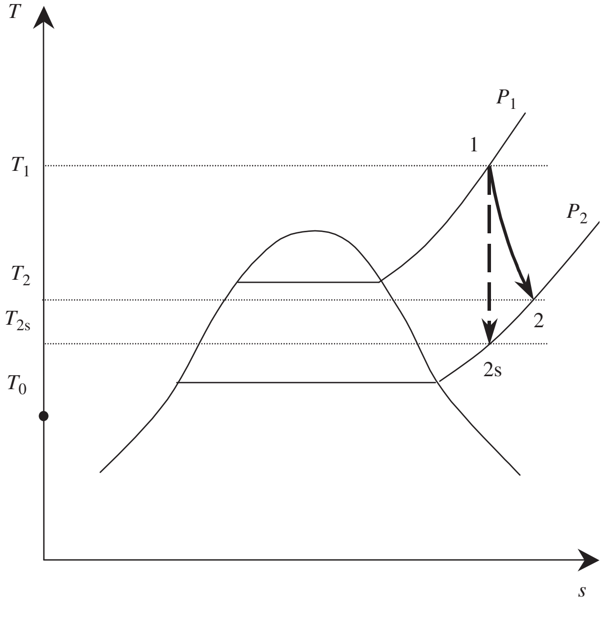


Fig. 2. For expansion efficiency definitions.

One may note that in this definition the reversible expansion from 1 to 2 would take place with an entropy increase, which can, for example, be obtained with simultaneous reversible addition of heat.

Although the Second Law efficiency, as defined by Eq. (38) is to our opinion valuable and is in frequent use, especially in the traditional thermodynamics work in Europe, it also has its detractors. The reservations are because it is not easy, and sometimes impossible, to uniquely define the appropriate reversible system (sometimes called the "reversible (or ideal) model") that corresponds to the real one that is being analyzed. Some examples of such model systems are discussed below.

4.2. *A starting case: a flow process between states 1 and 2*

Referring to Fig. 2 we examine the Second Law efficiency of the process 1→2, assuming a simple case of just work output and heat input. Following Eq. (6), here the energy efficiency is simply

$$\eta_{\mathrm{I}} \equiv \frac{W_u}{Q_{hp}} \tag{41}$$

and the efficiency of the process 1→2 when conducted reversibly is

$$\eta_{rev} = \left(\frac{W_u}{Q_{hp}}\right)_{rev}, \tag{42}$$

so

$$\eta_{\mathrm{II}} = \frac{W_u \big/ Q_{hp}}{W_{u,rev} \big/ Q_{hp,rev}} = \frac{W_u}{W_{u,rev}} \frac{Q_{hp,rev}}{Q_{hp}}. \tag{43}$$

For practical reasons (and without excluding any other uses of Eq. (43)) one most often compares the actual and reversible processes based on the same heat input,

$Q_{hp} = Q_{hp,rev}$, when Eq. (43) would then become

$$\eta_{\mathrm{II}} = \frac{W_u}{W_{u,rev}} = \frac{W_u}{(h_2 - h_1) - T_2(s_2 - s_1)}. \tag{44}$$

It is interesting now to compare this Second Law efficiency with the exergy efficiency for that process. Using the general equation (24) for this process to determine the exergy efficiency with a dead state choice of T_0 results in

$$\varepsilon_u = \frac{W_u}{A_{hp,i}} = \frac{W_u}{(h_2 - h_1) - T_0(s_2 - s_1)}. \tag{45}$$

Obviously, the Second Law and exergy efficiencies would be identical only if it is chosen that $T_0 = T_2$. It is thus also of interest to evaluate their relative values, viz.

$$\frac{\varepsilon_u}{\eta_{\mathrm{II}}} = \frac{[(h_2 - h_1)/(s_2 - s_1)] - T_2}{[(h_2 - h_1)/(s_2 - s_1)] - T_o}, \quad >1 \quad \text{for } T_2 < T_o; \quad <1 \text{ for } T_2 > T_o. \tag{46}$$

4.3. Single output simple power cycles

4.3.1. General definitions

The Second Law efficiency, Eq. (38), is used, and here the energy efficiency is simply

$$\eta_{\mathrm{I}} \equiv \frac{W_u}{Q_{hp}} \tag{47}$$

and the reversible cycle efficiency is

$$\eta_{rev} = \left(\frac{W_u}{Q_{hp}}\right)_{rev}, \tag{48}$$

so

$$\eta_{\mathrm{II}} = \frac{W_u \big/ Q_{hp}}{\left(W_u \big/ Q_{hp}\right)_{rev}} = \frac{W_u}{W_{u,rev}} \frac{Q_{hp,rev}}{Q_{hp}}. \tag{49}$$

As stated in the above section, for practical reasons one most often compares the actual and reversible processes based on the same heat input, $Q_{hp} = Q_{hp,rev}$,, hence Eq. (43) becomes

$$\eta_{\mathrm{II}} = \frac{W_u}{W_{u,rev}}. \tag{50}$$

To compute η_{II} (Eqs. (43), (50)), the cycle for which η_{rev} needs to be calculated must have a close relationship to the cycle under consideration, for which η_{I} is known, as stated at the outset. Starting with the work by Martinovsky [19,20] and Niebergall [21], the definition for that purpose of a "reversible model cycle" was advanced by Morosuk and co-workers [22,23] We now examine several cases for the definition of this reversible cycle.

4.3.2. Reversible systems in which the source and sink temperature are constant

A reversible cycle described by Fig. 3, operating between a high temperature isotherm T_h and a low temperature isotherm T_c, (the Carnot cycle) has a first law efficiency of $\eta_{\mathrm{I}} = W_u/Q_{hp}$, and a reversible cycle (Carnot) efficiency

$$\eta_{rev} = 1 - \frac{Q_o}{Q_i} = 1 - \frac{T_c(S_4 - S_1)}{T_h(S_3 - S_2)} = 1 - \frac{T_c}{T_h} \tag{51}$$

(because $S_4 - S_1 = S_3 - S_2$ by the cycle definition), and thus, from Eqs. (38), (41), and (51)

$$\eta_{\mathrm{II}} = \frac{W_u}{Q_{hp}\left[1 - (T_c/T_h)\right]}. \tag{52}$$

Although it looks like the expression for the exergy efficiency of the same cycle, Eq. (30), it differs from it in that the low isotherm T_c may be different, and usually is, from the dead state temperature T_0 chosen for the exergy analysis.

4.3.3. Example 1. For a system producing just power

A power engine absorbs heat $Q_h = 2000\,\mathrm{kJ}$ from a high temperature heat source ($T_h = 1000\,\mathrm{K}$) to produce power, and rejects $Q_c = 800\,\mathrm{kJ}$ to a low temperature heat sink (at $T_c = 303\,\mathrm{K}$), the environment temperature $T_e = 298\,\mathrm{K}$.

The net power output is thus

$$W_u = 2000 - 800 = 1200\,\mathrm{kJ}$$

and the energy efficiency according to Eq. (41) is

$$\eta_{\mathrm{I}u} = W_u/Q_{hp} = 0.60.$$

The plant operates between hot and cold reservoirs having temperature T_h and T_c, respectively. The exergy

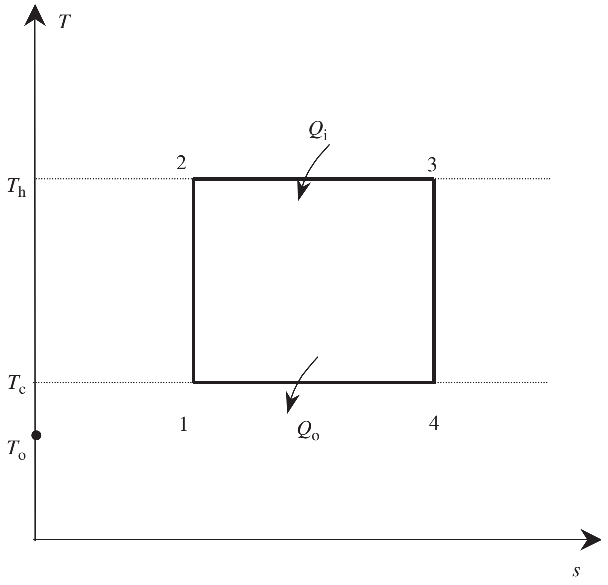


Fig. 3. Reversible system with constant source and sink temperatures (Carnot).

efficiency according to Eq. (30) is

$$\varepsilon_u = \frac{W_u}{Q_h\left[1-(T_e/T_h)\right]} = 0.855.$$

The Second Law efficiency is defined by comparison with an ideal plant working in between the same hot and cold reservoirs, and according to Eq. (52) is thus:

$$\eta_{\mathrm{II}} = \frac{W_u}{Q_{hp}\left[1-(T_c/T_h)\right]} = 0.861.$$

Because of the definition-based use of different reference systems, the exergy efficiency and the Second Law efficiency are different. They are identical to each other only for the specific case when the heat sink temperature T_c is identical to the environment temperature T_e.

4.3.4. Reversible systems with varying source and sink temperatures

In many power cycles the heat input and rejection is not even approximately isothermal. The reversible power cycle named after Lorenz [24] (Fig. 4) can serve as the "reversible (or ideal) model cycle" in such cases, and also serves well to introduce the "entropic temperature" concept useful in such analyses. This cycle consists of an isentropic compression stroke 1→2, followed by a stroke 2→3 in which heat is transferred to the working fluid at gradually increasing temperature till the top temperature T_3 of the cycle is reached, followed by an isentropic expansion stroke 3→4 to a lower pressure, and closed with a heat rejection stroke 4→1 at variable temperature. One case of the Lorenz cycle is the Brayton cycle (called by some the Joule cycle) in which the heat input and rejection strokes take place isobarically.

The equation of the first law efficiency of the Lorenz cycle remains the same as before, (41), but the reversible cycle efficiency, η_{rev} , defined as

$$\eta_{rev} = \frac{W_u}{Q_i} = \frac{Q_i - Q_o}{Q_i} = 1 - \frac{Q_o}{Q_i} = 1 - \frac{\int_1^4 T\,\mathrm{d}S}{\int_2^3 T\,\mathrm{d}S} \tag{53}$$

is a little more complex to calculate. A conceptual simplification is to express the efficiency of the Lorenz cycle in terms of an equivalent Carnot cycle operating between the temperatures $\hat{T}_h$ and $\hat{T}_c$, also known as the entropic temperatures, defined by

$$\hat{T}_h \equiv \frac{\int_2^3 T\,\mathrm{d}S}{S_3 - S_2} \qquad \hat{T}_c \equiv \frac{\int_1^4 T\,\mathrm{d}S}{S_4 - S_1}. \tag{54}$$

It is easy to show that the Carnot cycle operating between the temperatures $\hat{T}_h$ and $\hat{T}_c$ has the same efficiency as the Lorenz cycle described in Fig. 4, and the Lorenz cycle efficiency is thus

$$\eta_{rev,Lorenz} = 1 - \frac{\hat{T}_c}{\hat{T}_h}. \tag{55}$$

An alternate way to express Eq. (53), when the changes in the kinetic and potential energy, and work interactions, between states 1 and 4, as well as between 2 and 3, are negligible, is

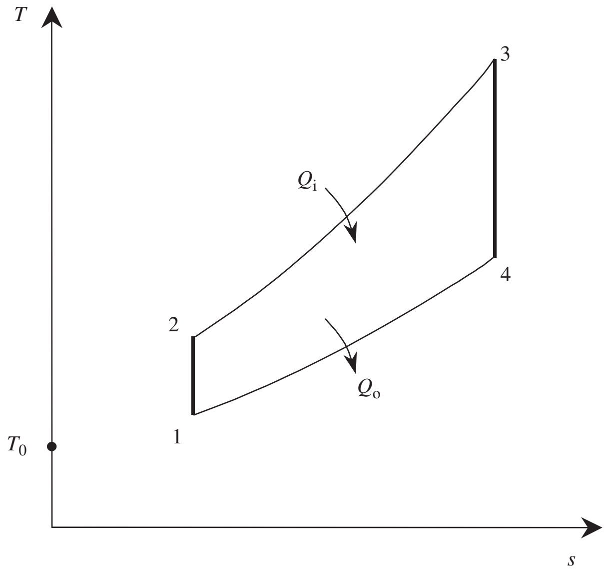


Fig. 4. Reversible systems with varying source and sink temperatures (Lorenz).

$$\eta_{rev} = 1 - \frac{Q_{4\to 1}}{Q_{2\to 3}} = 1 - \frac{\dot{m}_c(h_4 - h_1)}{\dot{m}_h(h_3 - h_2)}, \tag{56}$$

where for generality it is assumed that the mass flow rates in the heated and cooled strokes are different, $\dot{m}_h$ and $\dot{m}_c$, respectively. It is important to note at this point that the heat input $Q_{2\to 3}$ and the heat rejection $Q_{4\to 1}$ may either be calculated as the enthalpy changes of the working fluid of the cycle itself (then usually, when the working mass flow rate is the same in strokes 2→3 and 4→1, with, say, value $\dot{m}$, $\dot{m}_c = \dot{m}_h = \dot{m}$), or as the enthalpy changes of the heat source and sink fluids. In the latter case, the corresponding temperatures of the heat source fluids must be higher than the cycle fluid, $T_{f,2\to 3} > T_{2\to 3}$, and of the heat sink fluids must be lower than the cycle fluid, $T_{f,4\to 1} < T_{4\to 1}$, to allow heat transfer. It is also noteworthy that $Q_{f,2\to 3} = Q_{2\to 3}$ and $Q_{f,4\to 1} = Q_{4\to 1}$ only if there are no heat losses in these heat transfer processes.

Because $S_4 - S_1 = S_3 - S_2$ by the cycle definition,

$$\frac{\dot{m}_c}{\dot{m}_h} = \frac{s_3 - s_2}{s_4 - s_1}. \tag{57}$$

so substituting Eq. (57) into Eq. (56) gives

$$\eta_{rev} = 1 - \frac{(h_4 - h_1)/(s_4 - s_1)}{(h_3 - h_2)/(s_3 - s_2)} \tag{58}$$

and thus if the average temperatures of the Lorenz cycle are defined by Eq. (58) in the form of Eq. (54), we get

$$\hat{T}_h \equiv \frac{h_3 - h_2}{s_3 - s_2}, \quad \hat{T}_c \equiv \frac{h_4 - h_1}{s_4 - s_1} \tag{59}$$

and the efficiency of the Lorenz cycle is again expressed by Eq.(55).

Further simplification of Eq. (59) is possible, by expressing the enthalpies and entropies by the directly measurable properties such as T and p:

$$\mathrm{d}h = C_p\mathrm{d}T + [v - T(\frac{\partial v}{\partial T})_p]\mathrm{d}p \tag{60}$$

and

$$\mathrm{d}s = C_P\frac{\mathrm{d}T}{T} - (\frac{\partial v}{\partial T})_P\mathrm{d}p. \tag{61}$$

Integration of Eqs. (60) and (61), and substitution into Eq. (59) gives

$$\hat{T}_h = \frac{\int_{T_2}^{T_3} C_p\,\mathrm{d}T + \int_{p_2}^{p_3}[v - T(\frac{\partial v}{\partial T})_p]\,\mathrm{d}p}{\int_{T_2}^{T_3}\frac{C_p}{T}\,\mathrm{d}T - \int_{p_2}^{p_3}(\frac{\partial v}{\partial T})_p\,\mathrm{d}p}, \tag{62}$$

$$\hat{T}_c = \frac{\int_{T_1}^{T_4} C_p\,\mathrm{d}T + \int_{p_1}^{p_4}[v - T(\frac{\partial v}{\partial T})_p]\,\mathrm{d}p}{\int_{T_1}^{T_4}\frac{C_p}{T}\,\mathrm{d}T - \int_{p_1}^{p_4}(\frac{\partial v}{\partial T})_p\,\mathrm{d}p}. \tag{63}$$

In the case when $C_p = \text{const}$,

$$\hat{T}_h = \frac{C_p(T_3 - T_2) + \int_{p_2}^{p_3}[v - T(\frac{\partial v}{\partial T})_p]\,\mathrm{d}p}{C_p\ \ln(T_3/T_2) - \int_{p_2}^{p_3}(\frac{\partial v}{\partial T})_p\,\mathrm{d}p}, \tag{64}$$

$$\hat{T}_c = \frac{C_p(T_4 - T_1) + \int_{p_1}^{p_4}[v - T(\frac{\partial v}{\partial T})_p]\,\mathrm{d}p}{C_p\ \ln(T_4/T_1) - \int_{p_1}^{p_4}(\frac{\partial v}{\partial T})_p\,\mathrm{d}p}. \tag{65}$$

A further simplification is gained if the fluid is an ideal gas, following $pv = RT$ and thus $(\partial v/\partial T)_p = R/p = v/T$, then Eqs. (64) and (65) become

$$\hat{T}_h = \frac{C_p(T_3 - T_2)}{C_p\ \ln(T_3/T_2) - R\ \ln(p_3/p_2)},$$
$$\hat{T}_c = \frac{C_p(T_4 - T_1)}{C_p\ \ln(T_4/T_1) - R\ \ln(p_4/p_1)}. \tag{66}$$

Further, if the heat absorption and ejection processes are under constant pressure (like in the Brayton cycle), then $\mathrm{d}p = 0$. if C_p is constant, then we can get the following equation:

$$\hat{T}_h = \frac{T_3 - T_2}{\ln(T_3/T_2)}, \quad \hat{T}_c = \frac{T_4 - T_1}{\ln(T_4/T_1)}. \tag{67}$$

In this particular case, the efficiency of the Lorenz cycle is expressed as

$$\eta_{rev} = 1 - \frac{(T_4 - T_1)/\ln(T_4/T_1)}{(T_3 - T_2)/\ln(T_3/T_2)}. \tag{68}$$

Using Eqs. (43), (53), and (55), the Second Law efficiency based on the Lorenz cycle can be expressed as

$$\begin{aligned}\eta_{\mathrm{II}} &= \frac{W_u}{Q_{hp}(1 - Q_{4\to1}/Q_{2\to3})} \\ &= \frac{W_u}{Q_{hp}\left[1 - \left(\int_1^4 T\,\mathrm{d}S\Big/\int_2^3 T\,\mathrm{d}S\right)\right]} \\ &= \frac{W_u}{Q_{hp}(1 - \hat{T}_c/\hat{T}_h)}\end{aligned} \tag{69}$$

η_{II} defined by Eq. (69) is equal to the exergy efficiency ε of that system only if it is chosen that $T_0 = \hat{T}_c$.

4.4. Single output refrigeration cycles

4.4.1. COP-based Second Law efficiency

Refrigeration cycles are traditionally defined by the coefficient of performance [*COP*, Eq. (8)]. Consider a general refrigeration system operating on the paid energy inputs of heat Q_{hp} at temperature T_i and work W_p, to produce cooling of magnitude Q_{cu}, and heat Q_o is rejected at temperature T_o, as described in Fig. 5. The Second Law efficiency based on the *COP* would thus be defined as

$$\begin{aligned}COP_{\mathrm{II}} \equiv \frac{COP}{COP_{rev}} &= \frac{Q_{cu}\Big/\left(W_p + Q_{hp}\right)}{\left[Q_{cu}\Big/\left(W_p + Q_{hp}\right)\right]_{rev}} \\ &= \frac{Q_{cu}}{\left(Q_{cu}\right)_{rev}}\frac{\left(W_p + Q_{hp}\right)_{rev}}{\left(W_p + Q_{hp}\right)} \leq 1.\end{aligned} \tag{70}$$

The comparison between the actual and reversible cycles is often made based on the same useful cooling output for

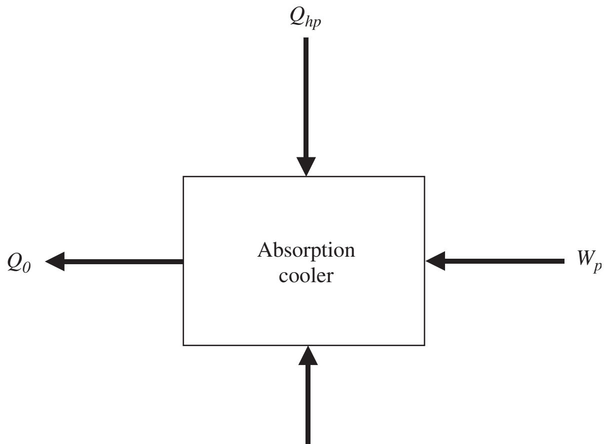


Fig. 5. Energy inputs and outputs for an absorption cooler.

both, $Q_{cu} = (Q_{cu})_{rev}$, and then Eq. (70) becomes

$$COP_{\mathrm{II}} = \frac{\left(W_p + Q_{hp}\right)_{rev}}{\left(W_p + Q_{hp}\right)} \leq 1. \tag{71}$$

After choosing an appropriate ideal model cycle one can calculate COP_{rev} (or the numerator of Eq. (71)) and thus COP_{II} when using Eqs. (70) or (71), respectively. A direct way leading to equations that allow the computation of COP_{rev} (and thus COP_{II}) without having to choose ideal model cycles, is based on the application energy and entropy balances to the system of Fig. 5, and several assumptions as shown below. From energy conservation

$$Q_{hp} + Q_{cu} + W_p - Q_o = 0. \tag{72}$$

The entropy balance for the reversible cycle $\Delta S = 0$, thus we can write

$$\left(\frac{Q_{hp}}{T_i} + \frac{Q_{cu}}{T_c} - \frac{Q_o}{T_o}\right)_{rev} = 0. \tag{73}$$

We note at this point that if these heat source and sink temperatures are not constant, the entropic temperature definition, Eq. (54), (or Eqs, (59) and (67)) can be used. Rearranging,

$$Q_o = W_p + Q_{hp} + Q_{cu}. \tag{74}$$

To simplify, and without loss of generality, it is reasonable to assume that the heat rejection is to the environment at the temperature of the environment, T_e, so $T_o = T_e$ and using this and Eq. (74) in Eq. (73) gives

$$\frac{Q_{hp}}{T_i} + \frac{Q_{cu}}{T_c} - \frac{Q_{hp} + Q_{cu} + W_p}{T_e} = 0 \tag{75}$$

or

$$Q_{cu}\left(\frac{T_e - T_c}{T_c}\right) - Q_{hp}\left(1 - \frac{T_e}{T_i}\right) - W_p = 0. \tag{76}$$

The terms in the parentheses are now named the reversible cycle efficiencies as follows:

$$\tilde{\eta}_{hp} \equiv 1 - \frac{T_e}{T_i}, \tag{77}$$

$$C\tilde{O}P_c \equiv \frac{T_c}{T_e - T_c}. \tag{78}$$

Using Eqs. (76)–(78) we can express the paid heat and work inputs required to produce the useful cooling output of the reversible cycle as

$$Q_{hp} = \left(\frac{Q_{cu}}{C\tilde{O}P_c} - W_p\right)\frac{1}{\tilde{\eta}_{hp}}. \tag{79}$$

Substituting Eq. (79) in the denominator of the COP_{rev} (shown in Eq. (70)) gives

$$COP_{rev} = \left[\frac{Q_{cu}}{\left(Q_{cu}/C\tilde{O}P_c\,\tilde{\eta}_{hp}\right) - W_p(1/\tilde{\eta}_{hp} - 1)}\right]_{rev} \tag{80}$$

and based on Eqs. (70) and (80) the Second Law COP is

$$COP_{\mathrm{II}} = \frac{Q_{cu}}{(Q_{cu})_{rev}} \frac{\left[\left(Q_{cu}/C\tilde{O}P_c\,\tilde{\eta}_{hp}\right) - W_p(1/\tilde{\eta}_{hp} - 1)\right]_{rev}}{\left(Q_{hp} + W_p\right)} \tag{81}$$

simplifying, if we assume for comparison that $Q_{cu} = Q_{cu,rev}$, to

$$COP_{\mathrm{II}} = \frac{\left(Q_{cu}/C\tilde{O}P_c\,\tilde{\eta}_{hp}\right) - W_{p,rev}(1/\tilde{\eta}_{hp} - 1)}{\left(Q_{hp} + W_p\right)} \tag{82}$$

All the terms on the right-hand side of this equation, except the required reversible work input $W_{p,rev}$, are known. If the latter can be estimated, COP_{II} can be calculated. One way to eliminate $W_{p,rev}$ from the equation is to express it in terms of Q_{hp} by assuming, for example, that the real and reversible cycle have the same W_p/Q_{hp} ratio.

Applying Eqs. (80) and (81) to the specific cases where the refrigeration cycle has only a work input (such as in vapor compression systems)

$$COP_{rev} = C\tilde{O}P_c = \frac{T_c}{T_e - T_c} \tag{83}$$

and

$$COP_{\mathrm{II}} = \frac{COP}{C\tilde{O}P_c} = COP\frac{T_e - T_c}{T_c}. \tag{84}$$

In another case when the required work input is negligible relative to the heat input (such as in absorption refrigeration systems),

$$COP_{rev} = C\tilde{O}P_c\,\tilde{\eta}_{hp} = \frac{T_c}{T_e - T_c}\,\frac{T_i - T_e}{T_i}. \tag{85}$$

That is a well-known expression, which for the more general case where the heat rejection temperatures in the absorber and condenser of the absorption cycle, T_a and T_{con}, are not identical, but under the idealized operation assumption that the solution concentration remains constant (infinitesimally small evaporation rates) and ideal heat recovery between the generator and absorber, making

$Q_a = Q_{hp}$, becomes (cf. [21])

$$COP_{rev} = \frac{\left[(1/T_a) - (1/T_i)\right]}{\left[(1/T_c) - (1/T_{con})\right]} \tag{86}$$

and corresponding to Eqs. (85) and (86) the equations in this case for COP_{II} are

$$COP_{\text{II}} = \frac{COP}{\tilde{COP}_c\ \tilde{\eta}_{hp}} \tag{87}$$

and

$$COP_{\text{II}} = COP\ \frac{(1/T_c) - (1/T_{con})}{(1/T_a) - (1/T_i)}, \tag{88}$$

respectively.

They differ from the expressions for the exergy *COP* of the same cycle, Eq. (31), in that the temperatures may be different, and usually are, from the dead state temperature T_0 chosen for the exergy analysis.

4.4.2. Example 2. For a system producing just cooling

In a vapor compression cooling system, the working fluid absorbs heat $Q_{cu} = 600\,\text{kJ}$ from a low temperature heat source (at $T_c = 200\,\text{K}$), and rejects heat $Q_e = 1000\,\text{kJ}$ to the environment, $T_e = 298\,\text{K}$,

The net power consumed is thus $W_p = 1000{-}600 = 400\,\text{kJ}$, and so from Eq. (9):

$$COP = Q_{cu}/W_p = 1.5.$$

If we assume that the dead state temperature T_0 is the same as the temperature of the environment, T_e, the exergy efficiency according to Eq. (31) is $\varepsilon_u = \left[\left(Q_{cu}(T_e - T_c)/T_c\right)/W_p\right] = 0.735$.According to Eqs. (83) and (84), $COP_{rev} = Q_{cu}/W_{p,rev} = T_c/(T_e - T_c)$ =2.04, and

$$COP_{\text{II}} = COP/COP_{rev} = 0.735.$$

It is found that the COP_{II} is the same as the exergy efficiency, because the system dead state temperature is chosen to be the environment temperature T_e; they would be different if the choice was different.

4.4.3. Reversible systems with varying source and sink temperatures

As in the case of power cycles discussed in Section 4.3.3, in many cooling cycles the heat input and rejection is not even approximately isothermal. The cooling cycle named after Lorenz (the reverse of the cycle in Fig. 4) is similarly used, and the entropic temperatures, defined for example by

$$\hat{T}_h \equiv \frac{\int_2^3 T\,\text{d}S}{S_3 - S_2}, \quad \hat{T}_c \equiv \frac{\int_1^4 T\,\text{d}S}{S_4 - S_1} \tag{89}$$

are substituted for the temperatures used in the equations in Section 4.4.1.

Simplifications of the entropic temperatures can be used, if appropriate, as those similar to Eqs. (54), (59) and (67).

4.5. Systems that simultaneously produce useful work, cooling and heating

In that case, and abbreviating the notations,

$$\eta_{\text{I}} = \frac{W_u + Q_{hu} + Q_{cu}}{Q_{hp}} = \eta_w + \eta_Q + COP_c, \tag{90}$$

where W_u, Q_{hu}, and Q_{cu} are the useful outputs of work, heat and cooling, Q_{hp} is the paid heat input to the cycle, and the efficiency terms on the right-hand side of the equation are defined as, the useful work production efficiency,

$$\eta_w \equiv \frac{W_u}{Q_{hp}}, \tag{91}$$

the useful heat production efficiency,

$$\eta_Q \equiv \frac{Q_{hu}}{Q_{hp}} \tag{92}$$

and the useful cooling output *COP*,

$$COP_c \equiv \frac{Q_{cu}}{Q_{hp}}. \tag{93}$$

It is noteworthy that all these efficiencies are normalized by the same total paid heat input Q_{hp} ignoring the fact that only some fraction of that heat input produces each of these outputs.

It is often of practical utility to define the ratios of the cooling and heating energy outputs to the work output, as

$$r_c \equiv \frac{Q_{cu}}{W_u}, \tag{94}$$

$$r_h \equiv \frac{Q_{hu}}{W_u} \tag{95}$$

and then Eq. (90) takes the form

$$\eta_{\text{I}} = (1 + r_c + r_h)\eta_w. \tag{96}$$

Eq. (96) is useful when comparing efficiencies of systems that have the same values of the output heat-work ratios r.

The reversible system efficiency can be expressed similarly as

$$\eta_{rev} = \left(\frac{W_u + Q_{hu} + Q_{cu}}{Q_{hp}}\right)_{rev} = \eta_{w,rev} + \eta_{Q,rev} + COP_{c,rev}, \tag{97}$$

where the efficiency terms on the right-hand side of the equation, all for the reversible case, are defined as follows:

the useful work production efficiency,

$$\eta_{w,rev} \equiv \frac{W_{u,rev}}{Q_{hp,rev}}, \tag{98}$$

the useful heat production efficiency,

$$\eta_{Q,rev} \equiv \frac{Q_{hu,rev}}{Q_{hp,rev}} \tag{99}$$

and the useful cooling output COP,

$$COP_{c,rev} \equiv \frac{Q_{cu,rev}}{Q_{hp,rev}}. \tag{100}$$

Similar to the energy balance shown in Fig. 1 but somewhat simplified for clarity, let us assume that a system produces useful work amount W_u, useful cooling Q_{cu} at temperature T_c, and useful heat Q_{hu} at temperature $T_{o,h}$, has a paid heat input Q_{hp} at temperature T_{hp}, and has "free" heat output to- and input from- the environment, $Q_{o,e}$ and $Q_{i,e}$ at temperatures $T_{i,e}$ and $T_{o,e}$, respectively. As done in Section 4.4.1, the entropy balance for this reversible cycle is

$$\left(\frac{Q_{hp}}{T_{hp}} + \frac{Q_{cu}}{T_c} + \frac{Q_{i,e}}{T_{i,e}} - \frac{Q_{hu}}{T_{hu}} - \frac{Q_{o,e}}{T_{o,e}}\right)_{rev} = 0 \tag{101}$$

and energy conservation

$$Q_{hp} + Q_{cu} + Q_{i,e} - Q_{o,e} - Q_{hu} - W_u = 0. \tag{102}$$

We note at this point that if these heat source and sink temperatures are not constant, the entropic temperature definition, Eq. (54) can be used. Combining Eqs. (101) and (102) to eliminate $Q_{o,e}$ yields

$$\begin{aligned} &- Q_{hp}\left(1 - \frac{T_{o,e}}{T_{hp}}\right) + Q_{cu}\left(\frac{T_{o,e} - T_c}{T_c}\right) + Q_{hu}\left(1 - \frac{T_{o,e}}{T_{hu}}\right) \\ &+ Q_{i,e}\left(\frac{T_{o,e} - T_{i,e}}{T_{i,e}}\right) + W_u = 0. \end{aligned} \tag{103}$$

The terms in the parentheses are now named the reversible cycle efficiencies as follows:

$$\tilde{\eta}_{hp} \equiv 1 - \frac{T_{o,e}}{T_{hp}}, \tag{104}$$

$$C\tilde{O}P_c \equiv \frac{T_c}{T_{o,e} - T_c}, \tag{105}$$

$$\tilde{\eta}_{hu} \equiv 1 - \frac{T_{o,e}}{T_{hu}}, \tag{106}$$

$$C\tilde{O}P_e \equiv \frac{T_{i,e}}{T_{o,e} - T_{i,e}}. \tag{107}$$

Using Eqs. (103)–(107) we can express the paid heat input required to produce the useful work, cooling and heating outputs of the reversible cycle as

$$Q_{hp} = \left(W_u + \frac{Q_{cu}}{C\tilde{O}P_c} + \tilde{\eta}_{hu}Q_{hu} + \frac{Q_{i,e}}{C\tilde{O}P_e}\right)\frac{1}{\tilde{\eta}_{hp}}. \tag{108}$$

Replacing the denominator in Eq. (97) with the last expression gives

$$\eta_{rev} = \frac{(W_u + Q_{hu} + Q_{cu})_{rev}}{(W_u + (Q_{cu}/C\tilde{O}P_c) + \tilde{\eta}_{hu}Q_{hu} + (Q_{i,e}/C\tilde{O}P_e))(1/\tilde{\eta}_{hp})}. \tag{109}$$

Similar to the derivation of Eq. (96), we define for the reversible cycle the heat-work output ratios as

$$\tilde{r}_c \equiv \left(\frac{Q_{cu}}{W_u}\right)_{rev}, \tag{110}$$

$$\tilde{r}_h \equiv \left(\frac{Q_{hu}}{W_u}\right)_{rev}, \tag{111}$$

$$\tilde{r}_e \equiv \left(\frac{Q_{i,e}}{W_u}\right)_{rev} \tag{112}$$

and with the substitution of Eqs. (110)–(112), Eq. (109) takes the form

$$\eta_{rev} = \frac{\tilde{\eta}_{hp}(1 + \tilde{r}_c + \tilde{r}_h)_{rev}}{1 + (\tilde{r}_c/C\tilde{O}P_c) + \tilde{\eta}_{hu}\tilde{r}_h + (\tilde{r}_e/C\tilde{O}P_e)}. \tag{113}$$

The Second Law efficiency is thus, using Eqs. (38), (90) and (97)

$$\eta_{\mathrm{II}} = \frac{\eta_w + \eta_Q + COP_c}{\eta_{w,rev} + \eta_{Q,rev} + COP_{c,rev}}, \tag{114}$$

or from Eqs. (96) and (113) gives another equation for η_{II} which is often easier to use:

$$\eta_{\mathrm{II}} = \frac{\eta_w(1 + r_c + r_h)}{\tilde{\eta}_{hp}(1 + \tilde{r}_c + \tilde{r}_h)}\left(1 + \frac{\tilde{r}_c}{C\tilde{O}P_c} + \tilde{\eta}_{hu}\tilde{r}_h + \frac{\tilde{r}_e}{C\tilde{O}P_e}\right). \tag{115}$$

All of the terms in Eq. (115) except $\tilde{r}_e$ are known from either choice or calculation, so if $\tilde{r}_e$ can be determined by some other means, η_{II} can be calculated.

Further simplification of efficiency comparisons is obtained if it is chosen that the heat-power outputs in the actual and reversible cycle are the same, $r_c + r_h = \tilde{r}_c + \tilde{r}_h$, and then Eq. (115) becomes

$$\eta_{\mathrm{II}} = \frac{\eta_w}{\tilde{\eta}_{hp}}\left(1 + \frac{\tilde{r}_c}{C\tilde{O}P_c} + \tilde{\eta}_{hu}\tilde{r}_h + \frac{\tilde{r}_e}{C\tilde{O}P_e}\right). \tag{116}$$

If it can be assumed that the heat exchange with the environment occurs at the temperature of the environment, T_e, so $T_{i,e} = T_{o,e}$, Eq. (116) becomes

$$\eta_{\mathrm{II}} = \frac{\eta_w}{\tilde{\eta}_{hp}}\left(1 + \frac{\tilde{r}_c}{C\tilde{O}P_c} + \tilde{\eta}_{hu}\tilde{r}_h\right) \tag{117}$$

and now η_{II} can be calculated without knowing $\tilde{r}_e$.

It is of interest to compare these Second Law efficiency equations with those defining the exergy efficiency presented in Section 3.

4.5.1. Example 3

This example demonstrates one possible error that can be made when the exergy and Second Law efficiencies are used interchangeably, without realizing their distinct definitions, using the case of a compound cycle for cogeneration of power, heating and cooling proposed by the authors [25]. The plant operates in a parallel combined cycle mode with an ammonia–water Rankine cycle and an ammonia refrigeration cycle, interconnected by the absorption, separation and heat transfer processes. It is driven by one external heat source fluid. In this paper, the heat source fluid is chosen to be air, entering the system at 465 °C/1.043 bar, and the net power output $W_u = 719$ kW. Both refrigeration and heating output are at variable temperatures. The refrigeration output $Q_{cu} = 266.2$ kW, the working fluid (rich ammonia stream) provide refrigeration in a evaporator at the temperature range of −22.7 °C to −15 °C and pressure of 1.6 bar, with the corresponding *entropic temperature* (Eq. (59)) $T_c = 250.5$ K. The heating fluid provide low level heat at the temperature range of 90–50 °C and pressure of 1.013 bar, the heat output $Q_{hu} = 308.9$ kW, at the corresponding *entropic temperature* $T_{hu} = 342.8$ K. The heating fluid finally exhausts to the environment ($T_e = 298.15$ K), and the heat addition process is also a temperature variable process, at the *entropic temperature* $T_{hp} = 492.5$ K. The total heat input $Q_{hp} = 3{,}496$ kW.

The first law efficiency [from Eq. (6)]:

$$\eta_{Iu} = \frac{W_u + Q_{hu} + Q_{cu}}{Q_{hp}} = 37.0\%. \tag{118}$$

Assuming that the exergy dead state temperature $T_0 = T_e$, the refrigeration exergy output is [Eq. (29)]

$$A_{cu} = Q_{cu}\left(\frac{T_e - T_c}{T_c}\right) = 50.6\,\text{kW}. \tag{119}$$

The heating exergy output is [Eq. (28)]

$$A_{hu} = Q_{hu}\left(1 - \frac{T_e}{T_{hu}}\right) = 40.2\,\text{kW}. \tag{120}$$

The exergy input is

$$A_{hp} = Q_{hp}\left(1 - \frac{T_e}{T_{hp}}\right) = 1379.6\,\text{kW}, \tag{121}$$

so, the exergy efficiency is [from Eq. (24)]:

$$\varepsilon_u = \frac{W_u + A_{hu} + A_u}{A_{hp}} = 58.7\%. \tag{122}$$

To calculate the Second Law efficiency, we should first find the first law efficiency of a reversible cycle, which operates under the same thermophysical conditions and, consistent with the derivations in this paper, we further choose one that has the same power, heating and cooling outputs. Using Eqs. (101) and (102) for this case:

$$\frac{Q_{hp,rev}}{T_{hp}} + \frac{Q_{cu}}{T_{cu}} - \frac{Q_{hu}}{T_{hu}} - \frac{Q_{e,rev}}{T_e} = 0,$$

$$Q_{hp,rev} + Q_{cu} = Q_{hu} + W_u + Q_{e,rev}, \tag{123}$$

where $Q_{e,rev}$ is the heat amount exhausted reversible to the chosen heat sink.

(1) If the heat sink is chosen to be the environment at $T_0 = T_\mathrm{e} = 298.15$ K, then we can calculate from Eqs. (123) that $Q_{hp,\ rev} = 2052.1$ kW, and the first law efficiency of the reversible system is thus:

$$\eta_{I,rev} = \frac{W_u + Q_{hu} + Q_{cu}}{Q_{hp,rev}} = 63.1\%$$

and the Second Law efficiency of the system is [Eq. (38)]

$$\eta_{II} = \eta_I/\eta_{I,rev} = 58.7\%.$$

In this case, the Second Law efficiency is the same as the exergy efficiency.

(2) If the heat sink temperature is chosen to be at a value different than the environment temperature T_e, for example, if the heat sink is sensibly assumed to be the cooling water at $T_0 = 303.15$ K, then $Q_{hp,\ rev} = 2108.4$ kW, and the first law efficiency of the reversible system is thus:

$$\eta_{I,rev} = \frac{W_u + Q_{hu} + Q_{cu}}{Q_{hp,rev}} = 61.4\%$$

and then the Second Law efficiency of the system is $\eta_{II} = \eta_I/\eta_{I,rev} = 60.3\%$, 2.7% higher than the exergy efficiency despite the smallness of the difference between the temperatures of the reference states (5 K, 1.6%).

5. Conclusions and recommendations

- There are many performance criteria for energy systems and they need to be defined and used with great care.
- The situation becomes especially complex when simultaneous energy interactions of different types, such as work, heating and cooling, take place with a system.
- The distinction between exergy and Second Law efficiencies is not clearly recognized by many.
- It is attempted here to clarify the definitions and use of energy and exergy based performance criteria, and of the Second Law efficiency, with an aim at the advancement of international standardization of these important concepts.
- Equations defining first law efficiencies including those considering embodied energy, environmental impact, and economics, and defining exergy and Second Law efficiencies for systems producing power, cooling, and cogeneration of power, heating and cooling are presented.
- Examples demonstrate some of the magnitude differences of exergy and Second Law efficiencies and the errors that can be made if the equations and systems are not defined carefully.

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Appendix A. A simple example of important differences in energy efficiency definitions

Take two ways that the energy efficiency is define, one, η_{1u} [Eq. (6)] subtracts the invested work (such as pumping, etc.) in the numerator, and the other, $\eta_{1u,d}$, adds it to the denominator instead. In the simplest form, the definitions are

$$\eta_{1u} = \frac{W_u - W_p}{Q_{hp}}, \tag{124}$$

$$\eta_{1u,d} = \frac{W_u}{Q_{hp} + W_p}, \tag{125}$$

It is of interest to know which of the definitions gives larger efficiency values than the other, so we examine the ratio

$$\begin{aligned}\frac{\eta_{1u}}{\eta_{1u,d}} &= \frac{(W_u - W_p)/Q_{hp}}{W_u/(Q_{hp} + W_p)} = \left(1 - \frac{W_p}{W_u}\right)\left(1 + \frac{W_p}{Q_{hp}}\right) \\ &= 1 + W_p\left(\frac{1}{Q_{hp}} - \frac{1}{W_u}\right) - \frac{W_p^2}{W_u Q_{hp}}.\end{aligned} \tag{126}$$

The last term is thus always negative, and the term before last is negative when $Q_{hp} > W_u$. Since the latter is always true thermodynamically, the conclusion is that $\eta_{1u}/\eta_{1u,d} < 1$. Thus one can say that defining the efficiency as η_{1u} is a more conservative evaluation of the efficiency, favoring in financial negotiations the system customer, and $\eta_{1,d}$ gives a higher value, thus favoring the system vendor.

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