Abstract

Limitations of energy conversion processes have been presented and after their discussion the exergy concept introduced using the most general definition of this thermodynamic quantity. Balancing exergy in processes differs from balancing procedures of energy so that the special behavior of exergy had to be stated and carefully considered. As a result the concept of exergy transition in a process could be introduced and on its base the generalized exergy rating quotient, the thermodynamic effectivity formulated. Some examples do illustrate its meaning and possibilities — from the quotient other widely used exergy efficiencies could be derived as special cases.

1 INTRODUCTION

Energy conversion processes can be balanced using the First Law of Thermodynamics. Appropriate rating quotients are always created in a subjective way. Although they are very easy to understand and very popular in the engineering practice, there are cases, in which they are not useful at all. That is why conversion processes are often analyzed using the exergy method. While the energy is converted from one kind to another, the exergy of the particular energy kind will be transformed either. Creating exergy rating quotients, however, is not that easy and in most cases it is not possible to do it on the subjective way alone. This makes problems in applying the exergy method so wide as it can be wished because of its important properties. Alas, these properties are not well known even by thermodynamicians. Following discussion should help avoid common mistakes in applying this valuable method.

2 ENERGY CONVERSIONS AND THEIR LIMITS

The First Law of Thermodynamics is a special case of the common Law of Energy Conservation. It is valid for all systems, in which the heat is determinable (in fact, it does not exist any heat definition), because of the number of particles in an analyzed system. In a system one kind of energy or energy interaction will be converted into another one. For the closed system as an energy converter there is

\[ dU_{\text{conv}} = dQ - pdV = dQ + dL. \]  

(01)
where e.g. the heat \( dQ \) will be converted into volume (absolute) work \( dL = -pdV \) at \( dU_{\text{conv}} = 0 \). The conversion of heat into work is the main process in the power engineering: its analysis was the basis for the development of thermodynamics since the 19th century. In the case of the flow system as an energy converter the *First Law* is

\[
dL_{\text{conv}} = dQ + Vdp = dQ + dL_t
\]

i.e. the heat \( dQ \) can be converted into technical (shaft or useful) work \( dL_t = Vdp \) at \( dU_{\text{conv}} = 0 \), where \( I = U + pV \) is the enthalpy, the quantity characterizing the flow system energy contents (or load).

The processes managed in the technological systems, either mechanical or process & chemical ones run always in the natural environment. This environment is an enough large system that does not change absorbing or supplying any thermodynamic quantity. Moreover, its intensities like the temperature \( T_0 \) and pressure \( p_0 \) do not vary in the time of analysis. Generally all energy conversion processes realized by the human take place in the natural environment, usually of the planet Earth.

Thus, there are some limitations of these conversions. They do not result from the *First Law*, but from the *Second Law of Thermodynamics*. The conversion of heat into volume (in the case of a closed system) or technical (in the case of a flow system) work is limited by the entropy balance. The system converting heat into work cannot be an entropy accumulator: the entropy supplied into it with the heat should be carried away, usually to the natural environment. If it is a natural process, i.e. an irreversible one, the irreversible entropy \( dS_{\text{irr}} \) will be produced according to the *Second Law*. Thus,

\[
dS_{\text{rev}} + dS_{\text{rev},0} + dS_{\text{irr}} = 0
\]

or, taking into account that the reversible entropy flow \( dS_{\text{rev}} \) is the so-called reduced heat \( dQ/T \),

\[
\frac{dQ}{T} + dS_{\text{rev}} + \frac{dQ_0}{T_0} = 0
\]

According to the *Second Law* there is always \( dS_{\text{irr}} > 0 \). In Eqs.(02)–(03) the heat to be converted is \( dQ \).

Additional heat–term is to be taken in the Equations, namely the heat \( dQ_0 \) resulting from Eq.(04), i.e. from the *Second Law*. It is the heat with which the entropy is carried out from the thermodynamic system to the natural environment.

A very similar dependence should be considered for the case of the volume (absolute) work, eventually created from the heat in the closed system. During this process system volume will change, i.e. it will increase continuously. To compensate this volume increase, which in fact will run till infinity, the converter should work in cycle (periodically) exchanging the compensating volume work with an outer system:

\[
dV + dV_0 = 0 \quad \text{or} \quad \frac{dL}{p} \frac{dT_0}{p_0} = 0
\]

where \( p_0 \) is the pressure of the compensating outer system, in the technological practice of the natural environment. Thus, Eqs.(01)–(02) should be completed to get

\[
dU_{\text{conv}} = dQ + dL + dQ_0 + dL_0; \quad dI_{\text{conv}} = dQ + dL_t = dQ + dQ_0 + dL_t
\]

Converting the heat \( dQ \) into work, some heat will be carried away to the natural environment of temperature \( T_0 \). For the volume compensation the work will be exchanged with the natural environment, either. Thus, the limitations in the natural environment as an outer reference system can be written down as follows, Eqs.(04)–(05):

\[
\frac{dQ}{T} + dS_{\text{irr}} + \frac{dQ_0}{T_0} = 0 \quad \text{and} \quad \frac{dL}{p} \frac{dT_0}{p_0} = 0
\]
From these limitations yields

\[ dQ_0 = -\frac{T_0}{T} dQ - T_0 dS^* \]  
and  
\[ dl_0 = -\frac{p_0}{p} dl \]  
(06)

The two energy interactions with the natural environment should be now taken into account in the energy balance of the conversion process of heat into work. For the closed system it will be at  
\[ dU_{\text{conv}} = 0 \]  
(no energy accumulation in the converter)

\[
dQ + dQ_0 + dl + dl_0 = \left(1 - \frac{T_0}{T}\right) dQ - T_0 dS^* + \left(1 - \frac{p_0}{p}\right) dl = 0
\]

and for the flow one at  
\[ dl_{\text{conv}} = 0 \]  
(no enthalpy accumulation in a converter)

\[
dQ + dQ_0 + dl = \left(1 - \frac{T_0}{T}\right) dQ - T_0 dS^* + dl_t = 0
\]

Hence, by the limitations presented above, the work (volume absolute or technical/shaft one) received from the heat  \( dQ \) is

\[
dl = -\frac{1}{1 - \frac{p_0}{p}} \left(1 - \frac{T_0}{T}\right) dQ + T_0 dS^*
\]  
(07)

and

\[
dl_t = \left(1 - \frac{T_0}{T}\right) dQ + T_0 dS^*
\]  
(08)

for the closed or the flow system, respectively. It is to emphasize the very popular mistake in the thermodynamics text–books, where in the last equation instead of the shaft (technical, useful) work the symbol  \( L \) for the absolute (or the so–called physical) work is applied. The volume work is a special case of the last kind of work (there are only two of them) and in the applied engineering thermodynamics is mainly denoted by the letter  \( L \). The CARNOT cycle (or heat engine) supplies the useful work. In fact physicists do not distinguish the two kinds of the work concept, or better to say: they mean only the absolute (or physical) work. On the contrary, for engineers the useful (technical or shaft) work  \( L_t \) is the most important kind of them both.

### 3 EXERGY CONCEPT

The revised definition of the thermodynamic quantity exergy is [1]

\[
exergy is the maximal part of energy (i.e. system energy or energy interaction), which in the presence of natural environment can be converted into any other kind of energy (i.e. system energy or energy interaction), especially into the useful work.
\]

In addition to it, the term maximal part is a requisite for reversible energy conversions. This definition is the most general one and, what should be stated, it links to the early–years exergy definitions, e.g. [2] (Die Exergie ist der in jede andere Energieform umwandelbare Teil der Energie; der Rest ist Anergie), [3]–[5], [6]–[8] (but also the critical review of the exergy theorems by R.W. Haywood, [9]). It allows building an easy understandable model of the exergy concept regarding its universal and univocal meaning*. The useful work, besides, is every kind of energy not characterized by entropy, which can be fully utilized, especially for practical (i.e. useful) purposes, e.g. [11]. It is the same as the technical or shaft work.

* Urged in some circles exergy definition, concerning only the system energy, originates back to J.H. KEENAN (Mechanical Engineering 54, 205/2032), who stated, that the availability of a fluid in a continuous stream is the maximum amount of useful work, which any heat engine, however simple or complex, can deliver against outside forces, to a shaft, by changing the condition of the flowing fluid to the dead state where  \( p=p_0 \),  \( T=T_0 \) and  \( u(velocity)=0 \), [10], p.136
According to the definition, from Eq.(08) becomes the heat exergy, i.e. the exergy of the heat flow $dQ$:

$$dE_Q = \left(1 - \frac{T_0}{T}\right) dQ = dL_t$$

(09)

By analogy the exergy of the volume absolute work can be determined (detailed derivation in [12]). Combining Eqs.(07)–(08) yields:

$$dE_L = \left(1 - \frac{p_0}{p}\right) dL = dL_t$$

(10)

The technical (or shaft) work is identical with the exergy: it is the exergy itself.

The heat and volume work exergies $dE_Q$ and $dE_L$ are the exergies of energy interactions heat $dQ$ and work $dL$. The interactions need an existence of the outer system to the analyzed (considered) one to be defined. But the energies characterizing closed and flow systems are inner energy and enthalpy. The question now is, what are their exergies, i.e. the exergy of the closed and of the flow systems (called exergy of the inner energy and exergy of enthalpy), respectively. Replacing the heat and volume work in Eq.(01) by their exergies, Eqs.(09)–(10), one becomes

$$dU = dQ + dL = dE_Q + \frac{T_0}{T} dQ + dE_L + \frac{p_0}{p} dL$$

and hence

$$dE_U = dE_Q + dE_L = dU - \frac{T_0}{T} dQ - \frac{p_0}{p} dL$$

or

$$dE_U = dU - T_0 dS + p_0 dV$$

The same derivations using Eq.(02) yields

$$dL = dQ + dL_t = dE_Q + \frac{T_0}{T} dQ + dL_t$$

$$dE_L = dE_Q + dL_t = dL - \frac{T_0}{T} dQ$$

and finally

$$dE_t = dL - T_0 dS$$

The last equation is often treated as a definition of the exergy concept.

In general, energy $W$ is a sum of exergy $E$ and anergy $A$, i.e.

$$W = E + A$$

which is called the First Law of Thermodynamics expressed by exergy. Using the above derived formulas for exergy of heat, volume work, inner energy and enthalpy, there is

$$dQ = dE_Q + dA_Q$$

$$dE_Q = \left(1 - \frac{T_0}{T}\right) dQ$$

$$dA_Q = \frac{T_0}{T} dQ$$

(11)

$$dL = dE_L + dA_L$$

$$dE_L = (1 - \frac{p_0}{p}) dL$$

$$dA_L = \frac{p_0}{p} dL$$

(12)

$$dU = dE_U + dA_U$$

$$dE_U = dU - T_0 dS + p_0 dV$$

$$dA_U = T_0 dS - p_0 dV$$

(13)

$$dL = dE_I + dA_I$$

$$dE_I = dL - T_0 dS$$

(14)

respectively. In the case of the technical (shaft) work there is obviously
The exergy is the thermodynamic property, which is every day used by power engineer (Der Energiebegriff des Energietechnikers und Energiewirtschaftlers deckt sich nicht mit dem Energiebegriff des Physikers, sondern weitgehend stimmt mit dem Exergiebegriff überein, e.g. [13]–[14]).

4 BALANCING EXERGY

From Eqs.(07)–(08) follows

\[
\begin{align*}
dL_t &= dE_{L_t} + dA_{L_t} \\
dL_t &= -dE_Q + T_0dS_{irr} \quad \text{and} \quad dL_t = -dE_Q + T_0dS_{irr}
\end{align*}
\]

With the same assumptions for the closed or flow system as an energy converter,

\[
\begin{align*}
dU_{conv} &= 0 \\
dS_{conv} &= 0 \\
dV_{conv} &= 0
\end{align*}
\]

or

\[
\begin{align*}
dL_{conv} &= 0 \\
dS_{conv} &= 0
\end{align*}
\]

yields

\[
\begin{align*}
dU_{conv} &= dQ + dQ_0 + dL + dL_0 = 0 \quad ; \quad dS_{conv} = \frac{dQ}{T} + \frac{dQ_0}{T_0} + dS_{irr} = 0 \quad ; \quad dV_{conv} = \frac{dL}{p} + \frac{dl_0}{p_0} = 0
\end{align*}
\]

or

\[
\begin{align*}
dL_{conv} &= dQ + dQ_0 + dL_t = 0 \quad ; \quad dS_{conv} = \frac{dQ}{T} + \frac{dQ_0}{T_0} + dS_{irr} = 0
\end{align*}
\]

and with Eq.(06)

\[
\begin{align*}
\left(1 - \frac{T}{T_0}\right)dQ + \left(1 - \frac{p_0}{p}\right)dL = T_0dS_{irr} \quad \text{or} \quad \left(1 - \frac{T}{T_0}\right)dQ + dL_t = T_0dS_{irr}
\end{align*}
\]

In the case, conditions according to Eqs.(15)–(16) are not valid, i.e. there is a system with accumulation, and

\[
\begin{align*}
dU_{conv} \neq 0 \\
dS_{conv} \neq 0 \\
dV_{conv} \neq 0
\end{align*}
\]

or

\[
\begin{align*}
dL_{conv} \neq 0 \\
dS_{conv} \neq 0
\end{align*}
\]

exergy balances for irreversible energy conversion processes in such a system can be obtained, viz.

\[
\begin{align*}
dE_{U} &= \left(1 - \frac{T}{T_0}\right)dQ + \left(1 - \frac{p_0}{p}\right)dL - T_0dS_{irr} \\
dE_{L} &= \left(1 - \frac{T}{T_0}\right)dQ + dL_t - T_0dS_{irr}
\end{align*}
\]

or, using other symbolic expressions,

\[
\begin{align*}
dE_{U} &= dE_Q + dE_L - T_0dS_{irr} \quad ; \quad dE_{L} = dE_Q + dL_t - T_0dS_{irr}
\end{align*}
\]

5 EXERGY AND IRREVERSIBILITIES

As it is to state from the Chapter 3, it cannot be formulated any exergy conservation law just like in the case of energy. In energy conversion processes exergy diminishes because of the irreversibilities. The term \(T_0dS_{irr}\) is the amount of exergy losses due to these irreversibilities. It was called sometimes the Law of Guy-Stodola (according to observations made by the French physicist and
later on by the Slovak engineer LOUIS GEORGES GOUY and AURELI STODOLA). But it leads to the conclusion that the exergy in processes converts into anergy in an irreversible way, i.e.

\[ E \rightarrow A \]

which is the Second Law of Thermodynamics expressed by exergy.

The most important term, however, is the so-called irreversible entropy production, which results from the Second Law. In Eq.(03) or Eq.(04) the terms \( dS_{\text{rev}}=dQ/T \) are parameters of state, but the \( dS_{\text{irr}} \) term does not. It cannot be proved using methods of the classical thermodynamics (the equilibrium one, for which the Zeroth Law of Thermodynamics is the main condition), but it can be stated without any doubts that \( dS_{\text{irr}} \) rises during the whole process, i.e. it increases with the time of the process run. In fact the time in the classical thermodynamics should be set equal to infinity, but one can imagine that the proportion can be written down as

\[ dS_{\text{irr}} \sim d\tau \quad \text{or} \quad \frac{dS_{\text{irr}}}{d\tau} > 0 \]

where \( dS_{\text{irr}}>0 \) (Second Law) and \( d\tau > 0 \) (the nature of time).

In the case on energy conversion processes one kind of an energy (or energy interaction) is converted into another one, e.g. the heat into work, or enthalpy into heat, etc. The total amount of energy at the start is the same as at the end of the process. In the case of exergy, however, there is a conversion of different kinds of exergies, but the difference between the sum of exergies at the start and at the end of the analyzed energy conversion process equals to \( T_0 dS_{\text{irr}} \). Thus,

\[ \sum_{\text{start}} W_{\text{start}} = \sum_{\text{end}} W_{\text{end}} \quad \text{and} \quad \sum_{\text{start}} E_{\text{start}} = \sum_{\text{end}} E_{\text{end}} + T_0 dS_{\text{irr}} \quad (20) \]

From these two balances can be stated that only in the case of the exergy one the overall rating quotient of the considered energy conversion process can be formulated in a univocal way, namely

\[ \eta_{\text{ex, total}} = \frac{\sum_{\text{end}} E_{\text{end}} - \sum_{\text{start}} E_{\text{start}}}{\sum_{\text{start}} E_{\text{start}}} \leq 1 \quad (21) \]

In the case of the energy balance according to Eq.(20) such an overall rating quotient always equals to one. That is why the formulation of energy rating quotients should be made in a subjective way. In the case of the exergy one, after the overall formula has been written down, some terms can be chosen in a subjective way either, depending on an experience, knowledge and goals intended by the investigator.

The creation of exergy rating quotients, i.e. quotients based on the exergy balance, makes very often troubles. In fact, they are usually formulated in the same way like the energy ones. That is why very often their numerical values are less than zero (negative) or greater than one, which is not logical and useful at all.

It is to state that because of the Law of Energy Conservation the sum of energies (or energy interactions) before the conversion process has been started equals to the sum of energies (or energy interactions) after the analyzed process has been occurred. In fact, there are no renewable energy resources at all: the energy amount does not change in processes, i.e. it cannot be made new. For every power engineer, however, the most important is the question: how much will cost a needed energy conversion. Only the sum of exergies at the start of an energy conversion process will be always less, at least by \( T_0 dS_{\text{irr}} \).

6 SPECIAL BEHAVIOR OF EXERGY TERMS

The terms of exergy balances, Eqs.(18)-(19), have some different behavior than the terms of energy balances. They change their algebraic sign while crossing the natural environment intensities \( T_0 \) or \( p_0 \). The basic expression for the heat exergy \( dE_Q \), Eq.(11), is a very characteristic case. Plotting the heat exergy against temperature (or heat temperature, i.e. the temperature at which the heat is sup-
plied to or carried away from the analyzed system) yields a non–monotonic function. Below the value $T_0$ (temperature of the natural environment) it falls down reaching zero just at $T_0$, and then, i.e. above $T_0$, it rises up. The functional dependence is very good known and has been presented many times in monographs on exergy method of thermodynamic analysis. But it has not been applied in the practice of the analysis. The fact is that the supplied heat below the temperature $T_0$ means diminishing exergy. If the heat $dQ$ is the supplied one (i.e. $dQ>0$) at $T<T_0$, its exergy is $dE_Q<0$, but above the $T_0$ temperature ($T>T_0$) its exergy rises, i.e. $dE_Q>0$.

It will be convenient to use some general symbols to make analyzes more clear and easier. Let the superscript $>$ means processes above and superscript $<$ processes below the limit $T_0$. Another symbol in subscript let be $+$ and $-$, whereby the first sign for supply and the second one for withdrawal. Thus, $dQ_+$ means heat supply and $dQ_-$ heat withdrawal. The appropriate heat exergies will be to

$$dE_{Q_+}^< < 0 \quad dE_{Q_+}^> > 0 \quad dE_{Q_-}^< < 0 \quad dE_{Q_-}^> > 0$$

The absolute volume work behavior will be the same because of the symmetry of Eqs.(11)–(12), i.e.

$$dE_L^< < 0 \quad dE_L^> > 0 \quad dE_{L_+}^< < 0 \quad dE_{L_+}^> > 0$$

but superscripts $<$ and $>$ do mean this time absolute volume work supply (subscript $+$) or withdrawal (subscript $-$) below or above the natural environment pressure $p_0$. The same behavior can be observed in the case of the two thermodynamic parameters of state $dE_U$ and $dE_I$, because they consist of two parts: the thermal and the mechanical one, i.e.

$$dE_U = dE_{U_T} + dE_{U_V} \quad \text{and} \quad dE_I = dE_{I_T} + dE_{I_p}$$

The special characteristics of exergy will be presented using perfect gas as a system. From Eqs.(13)–(14) there is

$$de_U = du - T_d s + p_v dv \quad \text{or} \quad de_I = di - T_p ds$$

and with $pv=RT$, $du=dq-pdv$ and $di=dq+vdp$ one becomes

$$de_U = \left(1 - \frac{T}{T_0}\right) c_v dT + \left(p_0 - RT_0 \frac{1}{v}\right) dv \quad \text{or} \quad de_I = \left(1 - \frac{T}{T_0}\right) c_v dT + \frac{RT_0}{p} dp$$

where from

$$de_{U,T} = \left(1 - \frac{T}{T_0}\right) c_v dT \quad \text{and} \quad de_{U,V} = \left(p_0 - RT_0 \frac{1}{v}\right) dv \quad \text{(22)}$$

$$de_{I,T} = \left(1 - \frac{T}{T_0}\right) c_v dT \quad \text{and} \quad de_{I_p} = \frac{RT_0}{p} dp \quad \text{(23)}$$

A very special behavior of the term $de_{U,V}$, especially for pressures below $p_0$ has been discussed in [15]. From above relations can be stated, that the inversion point of its change is to expect at

$$\frac{RT_0}{v} = p_0 \quad \text{or} \quad p_{T_0} = p_0 \quad \text{(24)}$$

where $p_{T_0}$ is the system pressure during its volume change at values $v$ and $T_0$; $p_0$ is the pressure of the natural environment. The terms $de_{U,T}$ and $de_{I,T}$, however, can be called thermal parts of the system exergy change.

The system exergy change can be parted into the thermal and mechanical exergy change, and it is up to the temperature or pressure (volume) range, where $T_0$ and $p_0$ do determine inversion points.
For example, during temperature rise, which can be caused by the heat supply, below $T_0$ the thermal part of the system exergy change decreases, but above $T_0$ increases, Eqs.(22)-(23). The mechanical part of the flow system exergy change, however, does not depend on the pressure range. The appropriate mechanical change for the closed system is not that interesting for the practice, although some interesting analyzes can be made. Thus, the exergy change of the flow system in the whole temperature (and pressure) range can be expressed by

$$E_{i2} - E_{i1} = -\left[\nabla E_{i1}^T + [\Delta E_{i1}^T] + [\Delta E_{i1}] \right]$$

for $dT>0$ (temperature rise), and

$$E_{i2} - E_{i1} = \left[\nabla E_{i1}^T - [\Delta E_{i1}^T] + [\Delta E_{i1}] \right]$$

for $dT<0$, with $dp>0$ in both cases. If there is $dp<0$, the term $[\Delta E_{i1}]$ should be replaced by $[\nabla E_{i1}]$.

The symbols $\Delta$ and $\nabla$ mean increase or decrease of the parameter of state and have been first used in [15]. Similar expressions can be obtained for the closed system, but for the mechanical (volume) part the inversion point, Eq.(24) should be taken into account.

7 THERMODYNAMIC TRANSITION

Because of the very large number of possible cases for both, the closed and the flow thermodynamic systems, there is a need of some rationalizations. Discussing only the most important for the practice flow systems, the general expression for the system exergy change between the states 1 and 2 can be written down as

$$E_{i2} - E_{i1} = -\left[\nabla E_{i1}^T + [\Delta E_{i1}^T] - [\Delta E_{i1}] - [\nabla E_{i1}] \right]$$

which includes Eqs.(25)–(26). The terms not concerning the analyzed case have to be set to zero.

The same „computer friendly” expressions can be formulated for the heat exergy $E_Q$, useful work $L_t$ (or the volume work $E_Q$). Hence, for a generalized flow system the appropriate thermodynamic transition can be formulated, i.e. Eq.(19) will be to

$$\begin{align*}
\left[\nabla E_{i1}^T \right] + \left[\nabla E_{i1} \right] + [E_{Qt}] + [E_{Qv}] + [L_t] & \rightarrow \\
\rightarrow \left[\Delta E_{i1}^T \right] + [\Delta E_{i1}] + [\nabla E_{i1}] & + [E_{Qt}] + [E_{Qv}] + [L_t] + T_0\Delta S_{irr}
\end{align*}$$

(27)

This approach has been used first in the research team of Professor WOLFGANG FRATZSCHER, a pioneer of the exergy method of thermodynamic analysis, e.g. [16]–[17] (as thermodynamischer Übergang), and later on proved many times in the practice of modeling, analysis and rating of energy conversion processes. The absolute value brackets have been used for convenience, although computing a particular term appropriate algebraic sign will be obtained automatically, which eases programming procedure.

Eq.(27) contains disappearing exergy terms $E_i^-$ in a process (left side) and the created $E_i^+$ in a process (right side). To the last terms refer also the irreversible exergy losses $T_0\Delta S_{irr}$. In general the thermodynamic transition for a particular process $m$ by means of the last equation can be written down as

$$\left(\sum_{j} E_{i}^-\right)_{m} \rightarrow \left(\sum_{i} E_{i}^+\right)_{m} + T_0\Delta S_{irr}$$

If a technological system containing $m$ processes is considered, appropriate terms will be added, and
\[
\sum_{m} \left( \sum_{j} E_{j}^{i} \right)_{m} \rightarrow \sum_{m} \left( \sum_{i} E_{i}^{i} \right)_{m} + T_{0} \Delta S_{m}
\]

where \( \Delta S_{m} \) is the total irreversible entropy production according to the Second Law.

8 THERMODYNAMIC EFFECTIVITY

Using the thermodynamic transition expression, general formula for the rating quotient on the exergy base can be obtained. The generalized exergy rating quotient, called thermodynamic effectiveness (in [16] the thermodynamische Effektivität), will be to

\[
\varepsilon = \frac{\Delta E_{T1}^{*} + \Delta E_{T1}^{*} + \Delta E_{Q1}^{*} + E_{Q1}^{*} + [L_{T1}]}{\sqrt{\Delta E_{T1}^{*} + \Delta E_{T1}^{*} + \Delta E_{Q1}^{*} + E_{Q1}^{*} + [L_{T1}]} \leq 1}
\]

Its numerical value is equal or less than 1 (because of process irreversibilities and thus, exergy losses) and equal or greater than 0. The above equation for a particular process \( m \) can be written as

\[
\varepsilon_{m} = \frac{\sum_{i} (E_{i}^{i})_{m}}{\sum_{j} (E_{j}^{i})_{m}}
\]

and for the system containing \( m \) processes

\[
\varepsilon_{S} = \frac{\sum_{m} \left( \sum_{i} (E_{i}^{i}) \right)_{m}}{\sum_{m} \left( \sum_{j} (E_{j}^{i}) \right)_{m}}
\]

Formulating the mathematical weight coefficient for disappearing exergy terms in a particular process \( m \) of the system,

\[
\gamma_{m} = \frac{\left( \sum_{i} (E_{i}^{i}) \right)_{m}}{\sum_{m} \left( \sum_{j} (E_{j}^{i}) \right)_{m}}
\]

the dependence of the thermodynamic effectiveness \( \varepsilon_{S} \) of the whole system on the particular process thermodynamic effectiveness \( \varepsilon_{m} \) can be obtained. It yields

\[
\varepsilon_{S} = \sum_{m} \left( \frac{\sum_{i} (E_{i}^{i})_{m}}{\sum_{m} \left( \sum_{j} (E_{j}^{i}) \right)_{m}} \right) = \sum_{m} \left( \frac{\sum_{i} (E_{i}^{i})_{m}}{\sum_{m} \left( \sum_{j} (E_{j}^{i}) \right)_{m}} \times \frac{\sum_{j} (E_{j}^{i})_{m}}{\sum_{m} \left( \sum_{j} (E_{j}^{i}) \right)_{m}} \right) = \sum_{m} \gamma_{m} \varepsilon_{m}
\]

Thus, the system thermodynamic effectiveness is a weighted average of thermodynamic effectiveness for particular system elements and the influence of every element on the system effectiveness is determined by its weigher \( \gamma_{m} \), independently on the system inner structure. The statement made above refers to the particular case of adiabatic multi-stage steam expansion exergy effectiveness presented by J.H. KEENAN (in the year 1932, [18]) and reported by V.M. BRODYANSKII [15]. This expansion in a three-stage turbine mentioned here is thus a real particular case of the thermodynamic effectiveness rating quotient application for power systems.
The more system elements, the greater the numerator and denominator in Eq.(29), thus, the less is the influence of an element onto the whole system perfection. This circumstance results from Eq.(30), because for weight coefficients the formal condition is valid

\[ \sum_{m} \gamma_m = 1 \]

Thus, the upper limit for numerical values of the complex system thermodynamic effectivity quotient is

\[ \lim_{m \to \infty} e_m = 1 \]

whereby \( \gamma_m \to 0 \), the lower limit (when only the system analyzed consists of only one element, i.e. of one process)

\[ \lim_{m \to 1} e_m = e_m \]

whereby this time there is \( \gamma_m \to 1 \). Dividing processes into stages should also result in better energy conversion, i.e. less relative irreversibilities.

The dependence problem of the element (or process) effectivity onto the whole system effectivity has been many times discussed in the subject literature. There could not be succeeded hitherto in working out a method (algorithm) for the generalized dependence of energy conversion process effectiveness as a system element on the effectiveness of the whole thermodynamic (power) system. The only exception is [19], but it refers to the very particular case, which cannot be generalized.

The experience in applying the thermodynamic effectivity rating quotient shows its main disadvantage: the numerical value is very often very close to one. To avoid it, the subjective way of choosing the terms is needed. The best way, however, especially analyzing huge technological systems is leaving the denominator of every thermodynamic effectivity quotient unchanged, choosing only appropriate terms of the nominator.

9 SOME EXAMPLES

Let’s apply above statements to a typical thermo–mechanical process of pressure changing in adiabatic and non–adiabatic turbines and compressors and throttling.

Power turbines do work usually adiabatic, so the thermodynamic transition, Eq.(27), will be to the exergy balance

\[ \nabla e_{LT}^{\infty} + \nabla e_{pl} \Delta e_{LT}^{\infty} + \Delta p_{LT} + T_0 \Delta e_{LT}^{\infty} \]

The terms \( \Delta e_{LT}^{\infty} \) and \( l_{LT} \) were also set equal to zero because they don’t concern the gas expansion process. During expansion the gas temperature gets lower which means that by temperatures above \( T_0 \) there is always \( \Delta e_{LT}^{\infty} = 0 \) and below \( T_0 \): \( \nabla e_{LT}^{\infty} = 0 \). Thus, the thermodynamic effectivity quotient is

\[ e_{dp=0, dq=0} = \frac{\Delta e_{LT}^{\infty} + l_{LT}}{\nabla e_{LT}^{\infty} + \nabla e_{pl}} \]

(31)

The particular forms of this quotient for the ranges above or under the natural environment temperature \( T_0 \) are

\[ e_{dp=0, dq=0}^{\infty} = \frac{l_{LT}}{\nabla e_{LT}^{\infty} + \nabla e_{pl}} = \frac{l_{LT}}{\nabla e_{pl}} \] and \[ e_{dp=0, dq=0}^{\infty} = \frac{\Delta e_{LT}^{\infty} + l_{LT}}{\nabla e_{LT}^{\infty} + \nabla e_{pl}} \]
The first quotient were very often presented in the literature as the exergy effectiveness of the gas expansion process in a turbine, but there wasn’t defined the appropriate temperature range under or above the \( T_0 \) temperature. Noting \( \tau_1 = T_1/T_0 \) and \( \tau_2 = T_2/T_0 \) as the perfect gas dimensionless temperatures at the start and at the end of a process, respectively, which can be calculated i.e. with a help of the isentropic (or adiabatic) effectivity, all the three presented quotients are to

\[
\varepsilon_{\text{dp}=0, dq=0}^{0} = \frac{\tau_1 - \tau_2}{\tau_1 - \tau_2 + \ln \frac{\tau_2}{\tau_1} - \frac{k-1}{k} \ln \frac{p_2}{p_1}}, \quad \varepsilon_{\text{dp}=0, dq=0}^{z} = \frac{\ln \frac{\tau_2}{\tau_1}}{\ln \frac{\tau_2}{\tau_1} - \frac{k-1}{k} m - 1} = \eta_{\text{polytropic}}
\]

where \( \eta_{\text{polytropic}} \) is the polytropic process effectivity, and in the case, the temperatures \( T_1 > T_0 \) and \( T_2 < T_0 \)

\[
\varepsilon_{\text{dp}=0, dq=0}^{0} = \frac{\tau_2 - 1 - \ln \tau_2}{\tau_1 - 1 - \ln \tau_1 - \frac{k-1}{k} \ln \frac{p_2}{p_1}}
\]

If \( \tau_2 = 1 \) (or \( T_2 = T_0 \)), the last of these three equations is identical with the first of them. The second equation, however, shows the independence of the thermodynamic effectivity value on process intensities — it depends only on the gas properties \((k)\) and irreversibilities, which are expressed by the polytropic (or more exact the pseudo–polytropic) exponent \( m \).

For non–adiabatic gas expansion processes the expression of the thermodynamic transition can be written as the exergy balance

\[
\nabla e_T^z + \nabla e_p^z + [e_Q^z, + e_Q^{z, -}] = \Delta e_T^z + [e_Q^{z, -}] + [e_L^z] + T_0 \Delta S_{\text{in}}
\]

and the appropriate thermodynamic effectivity quotient

\[
\varepsilon_{\text{dp}=0} = \frac{[e_Q^z] + [e_Q^{z, -}] + [e_L^z] + [\Delta e_T^z]}{[e_L^z] + [\nabla e_T^z] + [\nabla e_p^z]}
\]

When the heat delivered (subscript +) and carried away (subscript –) will be equal to zero, the above quotient will be the same as the Eq.(31). In the practical technology such a non–adiabatic process is to analyze in the refrigerating engineering as a process in so–called expansion engines. It takes places in the temperature range below the natural environment value \( T_0 \), where the heat is delivered. For such processes the thermodynamic effectivity quotient will be to

\[
\varepsilon_{\text{dp}=0, dq=0}^{0} = \frac{[e_Q^z] + [e_L^z] + [\Delta e_T^z]}{[\nabla e_T^z]}
\]

This form of the exergy rating quotient for the low temperature expansion engines are to be find among others in [15].

The expansion engines, however, very often do work in the temperature range which crosses the natural environment temperature \( T_0 \). The non–adiabatic behavior is a result of the temperature difference between the working agent and the natural surroundings. At temperatures above \( T_0 \) there is to observe the heat flow from the working agent to the surroundings and under the \( T_0 \) from the surroundings to the working agent. The expanding gas will change its temperature from the \( T_1 \) to \( T_0 \) and further to \( T_2 \). All the terms with superscripts \( > \) will be integrated in the limits from \( T_1 \) to \( T_0 \) and all the terms with superscript \( < \) from \( T_0 \) to \( T_2 \). Additionally \( e_Q^{z, -} = e_Q^z = 0 \) is taken into account. The thermodynamic effectivity of the process discussed will be therefore to
For the adiabatic compression process the appropriate thermodynamic transition will be to the exergy balance
\[
\dot{e}_{Q, \Delta q=0} = \frac{\varepsilon_0^\pi + \varepsilon_0^\pi_{\Delta q} + \varepsilon_0^\pi_{\Delta q} }{\nabla e_{T,T} + \nabla e_{T,T}^\pi}
\]
and the thermodynamic process effectivity in the whole temperature range
\[
\dot{e}_{\Delta p>0, \Delta q=0} = \frac{\Delta e_{T,T} + \Delta e_{T,T}^\pi + T_0 \Delta e_{\pi}}{\nabla e_{T,T} + \nabla e_{T,T}^\pi}
\]
whereby appropriate integrations are to be made between \(T_1\) and \(T_0\) or \(T_0\) and \(T_2\), if only the \(T_0\) value lies between the two process temperatures. It follows from the last equation for the range above \(T_0\):
\[
\dot{e}_{\Delta p>0, \Delta q=0} = \frac{\Delta e_{T,T} + \Delta e_{T,T}^\pi + T_0 \Delta e_{\pi}}{\nabla e_{T,T} + \nabla e_{T,T}^\pi}
\]
and for the temperature range below \(T_0\):
\[
\dot{e}_{\Delta p<0, \Delta q=0} = \frac{\Delta e_{T,T} + \Delta e_{T,T}^\pi + T_0 \Delta e_{\pi}}{\nabla e_{T,T} + \nabla e_{T,T}^\pi}
\]
The first of the two last rating quotients is the usually formulated in the literature exergy effectiveness of the adiabatic compression process, e.g. [15]. For the perfect gas as working fluid one gets (by \(T_1=T_0\)):
\[
\dot{e}_{\Delta p=0, \Delta q=0} = \frac{T_0 \ln \frac{T_2}{T_0} - \frac{k-1}{k} \ln \frac{p_2}{p_1}}{T_2 - T_0} = 1 - \ln \frac{\tau_2}{\tau_1} = 1 - \frac{\ln \tau_2 - \frac{k-1}{k} \ln \pi}{\tau_2 - 1}
\] (33)
or assuming a polytropic process (for \(T_1=T_0\), as well),
\[
\dot{e}_{\Delta p=0, \Delta q=0} = 1 - \left( \frac{m-1}{m} - \frac{k-1}{k} \right) \frac{\ln \pi}{\frac{m-1}{\pi} = -1}
\]
where \(\pi\) equals to \(p_2/p_1\). For the compression process below the natural environment temperature \(T_0\) one gets
\[
\dot{e}_{\Delta p<0, \Delta q=0} = \frac{k-1}{k} \frac{m}{m-1} = \eta_{\text{polytropic}}
\]
This result was obtained by assuming the polytropic compression process. In fact, the assumed polytropic process is the so-called pseudo–polytropic one, because the exponent \(m\) gives the information about process irreversibilities (irreversible adiabatic process). In the same way the thermodynamic effectivity of the adiabatic expansion process of the perfect gas was equal to the polytropic effectiveness. For the adiabatic compression, however, the \(\eta_{\text{polytropic}}\) value changes in the range between \((k–1)/k\) and 1, [20].

For the general case \(T_1\neq T_0\) and perfect gas as working fluid the thermodynamic effectivity by \(T_1<T_0\) but \(T_2>T_0\) it becomes
\[
\varepsilon_{\Delta p,0,\Delta q=0} = \frac{k-1}{k} T_0 \ln \frac{P_2}{P_1} + (T_2 - T_0) - T_0 \ln \frac{T_2}{T_0} \quad \frac{k-1}{k} \ln \frac{r_2 - 1 - \ln r_2}{r_2 - 1 - \ln r_2}
\]

and by \( T_0 > T_0 \)

\[
\varepsilon_{\Delta p,0,\Delta q=0} = \frac{T_0}{T_0} \ln \frac{T_2}{T_0} - \frac{k-1}{k} T_0 \ln \frac{P_2}{P_1} = \ln r_2 - \frac{k-1}{k} \ln \frac{r_2}{r_1}
\]

If only \( T_1 = T_0 \) (or \( T_1 = 0 \)) the last formula will be the same as the quotient obtained for such a case above, Eq.(33), because the natural logarithm of one equals to zero.

The thermodynamic transition for compression processes above \( T_0 \) with concurrent cooling by \( T_1 \) is to the exergy balance

\[
\sum_{i} \dot{q}_i = \dot{e}_{\text{expl}} + \Delta e_{\text{rr}} + \Delta e_{\text{ex}} + T_0 \Delta s_{\text{w}}
\]

and the appropriate thermodynamic effectiveness quotient

\[
\varepsilon_{\Delta p,0,\Delta q=0} = \frac{\dot{e}_{\text{expl}}}{\dot{f}_{\text{ex}}}
\]

(34)

For the isothermal compression at \( T_0 \) in the same way the quotient

\[
\varepsilon_{\Delta p,0,\Delta q=0} = \frac{\Delta e_{\text{rr}}}{\dot{f}_{\text{ex}}}
\]

(35)

can be obtained, which corresponds to the exergy effectiveness quotients formulated e.g. in [15]. It was proposed (e.g. in [15]) as the general exergy rating quotient for gas compression processes of all kinds. But, if only the analyzed isothermal process runs above the natural environment temperature \( T_0 \), than from the Eq.(34) yields

\[
\varepsilon_{\Delta p,0,\Delta q=0} = \left( 1 - \frac{T_0}{T} \right) + \frac{\Delta e_{\text{rr}}}{\dot{f}_{\text{ex}}}
\]

(36)

So, the Eq.(35) is the special case of the last expression, when only \( T > T_0 \) (especially \( T > T_0 \)).

Throttling processes, as a pressure fall without work producing ones, can be analyzed in the same way. Only the JOULE–THOMSON coefficient \( k_{\text{J–T}} \) should be taken into account, [15]. From Eq.(32) follows in the case of adiabatic throttling process considering \( k_{\text{J–T}} > 0 \) (which means \( d\tau < 0 \))

\[
\varepsilon_{\Delta p} = \frac{\Delta e_{\text{rr}}}{\nabla e_{\text{rr}} + \nabla e_{\text{ex}}}
\]

After \( \Delta T \) for given \( \Delta p \) has been determined as for real gas, perfect gas formulas can be applied for computing appropriate exergy changes — such an approach makes process modeling easier without any remarkable results precision (especially by modeling huge power engineering systems).

10 CONCLUSIONS

Presented approach to the exergy concept shows many additional problems that could not be solved in a satisfactory way until now, but it points to the new powerful possibilities of the exergy method of thermodynamic analysis. Especially the creation of exergy rating quotients has been finally cleared and an appropriate algorithm for the most important power engineering processes derived. It can be widened for all kinds of energy or substance conversions. The graphical interpretations of the approach presented in this paper contain Figures 1 and 2. Besides, the coupled thermodynamic systems can be analyzed, e.g. thermally coupled by heat \( dQ \), transforming \( dL \) into \( dL_0 \), [20]–[21].
Fig. 1 Energy converter as a simple thermo–mechanical closed and flow system without accumulation

Fig. 2 Energy converter as a simple thermo–mechanical closed and flow system with accumulation

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