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THERMODYNAMICS OF DEVELOPMENT OF ENERGY SYSTEMS WITH APPLICATIONS TO THERMAL MACHINES AND LIVING ORGANISMS

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Abstract

We define and analyse thermodynamic limits for various traditional and work-assisted processes of sequential development with finite rates important in engineering and biology. The thermodynamic limits are expressed in terms of classical exergy change and a residual minimum of dissipated exergy, or some extension including time penalty. We consider processes with heat and mass transfer that occur in a finite time and with equipment of finite dimension. These processes include heat and separation operations and are found in heat and mass exchangers, thermal networks, energy converters, energy recovery units, storage systems, chemical reactors, and chemical plants. Our analysis is based on the condition that in order to make the results of thermodynamic analyses usable in engineering economics it is the thermodynamic limit, not the maximum of thermodynamic efficiency, which must be overcome for prescribed process requirements. A creative part of this paper outlines a general approach to the construction of 'Carnot variables' as suitable controls. Finite-rate, endoreversible models include minimal irreducible losses caused by thermal resistances to the classical exergy potential. Functions of extremum work, which incorporate residual minimum entropy production, are formulated in terms of initial and final states, total duration and (in discrete processes) number of stages.

Keywords: Carnot cycle, exergy, finite-time thermodynamics, heat pumps, thermal engines.

1. Introduction: Thermodynamic Limits by Optimization

Recently a unifying concept of the dynamical (finite rate) limits for energy production or consumption has been proposed, both in thermal engineering and ecology [1]–[3]. The integrating nature of these limits is important. Traditional engineering approaches to exchange and separation processes dissect, in fact, the field on the basis of what is specific for individual processes (or systems) rather than integrate these individual processes. One of the major aims of analyses based on integrated limits is to work out such conceptual approaches that could lead an engineer to certain generic rather than specific limits or bounds on practical or industrial processes. They describe largely dynamic limits that exhibit a significant degree of universality. Such limits are not only stronger than static, the consequence of finite rates, but are also more useful in design. Our interest here is in revealing and systematising such generic limits. They may, for example, determine a lower bound for the amount of the energy supply, exploitation costs, amount of a key substance, investment, equipment dimension, etc. Still, the bounds we are looking for are not classical bounds encountered in textbooks on thermodynamics and separation science. Those classical bounds pertain to reversible and infinitely slow processes. They are often unrealistically low and hence, very often, useless.

We are interested in 'dynamic' bounds of physical origin – usually functions of operational constraints – established under the condition that, in any circumstances, the process will run with a minimum required intensity, yet yielding a desired product. This requirement usually yields bounds that are orders of magnitude higher than those classical ones known from the textbooks. Complex optimization techniques must be used to obtain dynamic limits for various processes, including those in exchange and separation systems. The conceptual machinery of Finite Time Thermodynamics (FTT) and Optimal Control Theory (OCT) that derives these limits has recently found pronounced applications in design of solar engines, solar cells, semiconductor devices, photosynthesis engines and other sophisticated devices, see, e.g., a book of De Vos 1992 [1].

Traditionally, energy limits are derived from exergy analyses that often deal with thermal systems composed of many objects and links and include ecological applications of exergy. A basic notion therein that is supposed to be of value in thermal technology is the so-called cumulative exergy cost defined as the total consumption of exergy of natural resources necessary to yield the unit of a final product [2]. Also introduced is the notion of cumulative exergy loss, as the difference between the unit cumulative exergy consumption and exergy of the considered product. In ecology, ecological counterparts of these quantities are introduced. Consequently, in ecology, the ecological cost is used as the cumulative consumption of exergy of unrestorable resources burdening a definite product. Also, so-called pro-ecological tax can be imposed as the penalty for negative effects of action causing exhaustion of natural resources and contamination of natural environment [2]. All these applications involve non-equilibrium processes in which the use of the sole notion of the classical exergy is insufficient without including the associated notion of minimal (residual) dissipation of this exergy.

Dynamic energy limits are, in fact, the realm into which we are driven with many analyses that lead to non-equilibrium applications of the exergy. They emerge since engineering processes must be limited by some irreversible processes allowing a minimum entropy production rather than by purely reversible processes. However, these limits cannot be evaluated from the method of cumulative exergy costs [2], as it has its own imperfections and disadvantages. Its definition of the sequential process, no matter how carefully made, is vague. The total consumption of exergy of natural resources, necessary to yield a product which defines the cumulative exergy cost, is burdened by sorts, locations and dates of various technologies, the property that usually changes process efficiencies, semiproducts, controls, etc., and thus influences the cost definition. One way to improve the definition would be to deal with statistical measures of the process and its exergy consumption. Yet, a statistical procedure leading to an averaged sequence process, that would add the rigor to the definition of cumulative exergy costs, is not defined in the original work [2]. Moreover, in the current definitions of the cumulative exergy cost and ecological cost, the mathematical structures of these costs and related optimal costs remain largely unknown. In fact, cumulative costs are not functions but rather functionals of controls and state coordinates, only optimal costs have properties of functions (potentials). To ensure potential properties for costs, their definition should include a method that would eliminate the effect of controls. Yet, the original definition of the cumulative exergy cost [2] does not incorporate any approach of this sort, the property that makes this definition inexact. On the other hand, in FTT [3], suitable cost functions can be found via an optimization as exact potentials.

2. Potential Functions of Diverse Engineering Operations

Suitable averaging procedures were proposed along with methods that use averaged criteria and models in optimization [3]. Most importantly, it was shown that any optimal sequential process has a quasi-Hamiltonian structure that becomes Hamiltonian in the special cases of processes with optimal dimensions of stages and in limiting continuous processes [3], [4]. This means that the well-known machineries of Pontryagin's maximum principle [5] and dynamic programming [6] can effectively be included to generate optimal cost functions in an exact way [3], [4]. Finally these theoretical achievements were transferred into the realm of operations governed by economical criteria [3]. Yet, bounds or limits on the energy consumption must be defined as purely physical quantities, independent of economical properties of the operation [4].

All classical measures of thermodynamic perfection, such as the Carnot efficiency, exergy efficiencies or dissipated exergy, have one characteristic in common: they all take the reversible process as their reference [7], [8], [9]. In irreversible approaches the thermodynamic bounds are defined by the minimal value of the total exergy driving a finite time process [10]. FTT investigates the effects of constraints on time and rate on the optimal performance of generic processes through integral or sum expressions describing various criteria, e.g. $\sum \Delta S_k^i$, $\sum \Delta B_k^{in}$, W, or their generalizations including time-like variables. Usually the goal of an FTT analysis is:

1. to find the paths of minimum $\sum \Delta B_k^{in}$ or $\sum \Delta S_k^i$ for the purpose of finding realistic bounds on consumption of energy and resources in thermal, separation and chemical reaction processes (here the ones incorporating the minimal necessary irreversibility),
2. to find the optimal strategies or controls for such processes, and
3. to refer these bounds to an actual process to verify its possible improvement.

The bounds constructed on the basis of thermodynamic criteria, in particular exergy, are both relevant and useful; exergy is a unique common measure of various resources and energy. They define thermodynamic limits rather than the economic consumption of exergy or resources for various generic processes. Optimization techniques play a central role in obtaining the majority of bounds in FTT. The methods of linear programming [11] and nonlinear programming [12] are as a rule insufficient in those situations where functional extrema are sought. Instead, the application of optimal control techniques is necessary [13]–[15]. FTT retains the philosophy of model idealization known from reversible thermodynamics (the Carnot cycle) but uses somewhat more realistic models which have some basic irreversibilities incorporated [16], [17].

The solution of a thermo-economic problem is, in general, not equivalent to that of the corresponding thermodynamic problem. It does, however, reduce to thermodynamic optimizations in two special cases. The first case appears when the price of certain thermodynamic quantities such as the power produced becomes much larger than the prices of other participating quantities [18]. This limit represents an energy theory of value, i.e. a value system in which one considers energy as the single valuable commodity [19]. In the second case the economic value of the exergy unit is the same for all forms of matter and energy taking part in the process. Then the thermodynamic problem of the minimum exergy loss is equivalent to that of the minimum of the economic costs. This case is however quite special since the prices of the exergy units generally differ [20].

From the standpoint of thermoeconomics, optimization of the driving exergy (exergy costs K) is admissible only after a fixed system structure has been reached. This is because these costs can at best only approximate the exploitation costs under the assumption of a single exergy unit and for a constant investment. Yet, an approximate optimization of the tradeoff between investment costs and exergy based exploitation costs can offer useful estimates. This was summarised by various researchers [20]–[23]. On the other hand, approaches to 'optimal design' that use the entropy (or exergy) generated as their optimization criteria make little sense from the standpoint of thermoeconomic design.

CURZON and AHLBORN [1], [16] analyzed power yield with Newtonian heat exchange; models with various functional forms of the temperature difference have also been designed [24]. Of practical importance is radiative heat transfer, where the heat flux is proportional to temperature to the fourth power. Another case is derived from linear irreversible thermodynamics and considers the reciprocal temperature difference. These investigations show that the CURZON and AHLBORN formula is not always simply a function of the reservoir temperatures, T_2 and T_1. It depends, in general, on other variables such as the reservoir heat capacity (for finite reservoirs, see ref. [25]) or the specific heats of the working fluid. This efficiency is not a fundamental upper limit for engines working at maximum power; it depends on the functional temperature dependence of the heat exchange between the working fluid and reservoirs. Moreover, real heat engines with friction and heat leaks exhibit fundamentally different power-efficiency curves than those in which finite-rate heat transfer is the only irreversibility. The presence of friction leads to higher efficiencies when the machine operates more slowly, and heat leaks lead to higher efficiencies when the machine operates at faster rates. It follows that optimization automatically sorts heat engines into two distinct classes, those dominated by heat leaks and those dominated by friction [26]–[29]. These analyses showed that the time of the absorbing heat process must be longer than that of the releasing one in the Onsagerian case, but that the times of the two heat exchange processes should be the same for Newton's law of heat transfer.

The exergy and heat consumed in separation units can now be treated in general terms without reference to any specific process, whether it be distillation, desorption, or drying. This leads to limits on the performance of separation processes [30]. For a given separation effect the lowest bound for heat consumption is determined by thermostatics and is given by the ratio of the minimum work of separation to the related Carnot efficiency. However, this limit is unrealistically low, and, more importantly, it does not correspond to any real feed flow. An irreversible bound on the heat consumed in separation processes has been determined as a function of feed flow [30] and gives a more realistic limit. For any finite rate separation process with a given finite mass flow (average mass flow in the case of cyclic processes) the exergy consumption is larger than the corresponding reversible consumption. This bound is a function of the flow F. Knowledge of this bound is of value for design. The difference between bounds and the actual heat consumption can be illustrated by an example of the economic design of a typical rectification column [31]. The tradeoff between the operational and investment costs results in the economical reflux, usually several times larger than the lowest possible one. In the rectification column the consumption of heat supplied to the boiler grows linearly with the reflux R; $Q = D(R+1)r$, where r is the average heat of evaporation and D is the flow of distillate. The actual heat is then several times larger than the lowest possible one corresponding to the bound of minimum entropy production. In effect, real columns are never designed to operate at the bound of minimum heat or minimum σ even if this is an FTT limit.

As no limits are imposed on the use of renewable energy sources, the operations that exploit these sources are often economically realistic. This stimulates operations with biomass, wind energy, solar energy (photothermal and photovoltaic converters), energy of waterfalls, waves and tides, geothermal energy and convective-hydrothermal resources [32]–[34]. Photothermal and photovoltaic conversions have been treated by LANDSBERG [35] and JARZEBSKI [36], and, in the framework of FTT, by DE VOS [1]. The solar driven convection known as winds has been modelled in terms of the FTT of heat engines by treating the Earth's atmosphere as the working fluid [1], [24]. Upper and lower limits for the coefficient of performance of solar absorption cooling cycles have been derived from the first and second laws [37]. However, most chemical processes consume unrestorable natural resources; the quicker civilization develops, the sooner these are exhausted. Exergy can be used as a measure of the quality of these resources [2], [38]–[40]. It is important to calculate the rate at which industrial processes consume exergy resources. The cumulative consumption of exergy from unrestorable natural resources appearing in the chain of processes leading from natural raw materials to product expresses the ecological cost of the product [38], [39], [41]–[46]. Cumulative exergy cost seems to be suitable for industrial chemistry. However, it is neither a true cost nor a proper measure of energy limits since these latter are purely physical quantities. In fact, as stated in Sec.1, the method of cumulative exergy costs has serious imperfections. These are:

a. vague sequential process;
b. date- and location-affected exergy consumption of resources defining cumulative cost,
c. undefined mathematical structure of costs.

To ensure potential properties for cumulative costs, their definition must eliminate the effect of controls. This is ensured in the method that deals with *optimized* costs as physical energy limits, discussed below.

3. Physical Energy Limits for Sequential Exchange Operations

In this work we expose several basic expressions which quantify limits on production or consumption of mechanical energy in operations with heat and mass exchange. Our method generalises the well-known method of evaluation of the classical exergy in reversible sequences [46], [47]. The problem of finite-rate limits, briefly outlined in an earlier paper [48], requires sequential operations with thermal machines [49]–[51], such as multistage heat pumps. For the case of energy consumption, total power input is minimized at constraints that describe dynamics of energy and mass exchange. The results are limiting work functions in terms of end states, duration and (in discrete processes) number of stages [51], [52]. For the case of energy production (*Fig. 1*) total power input is maximized.

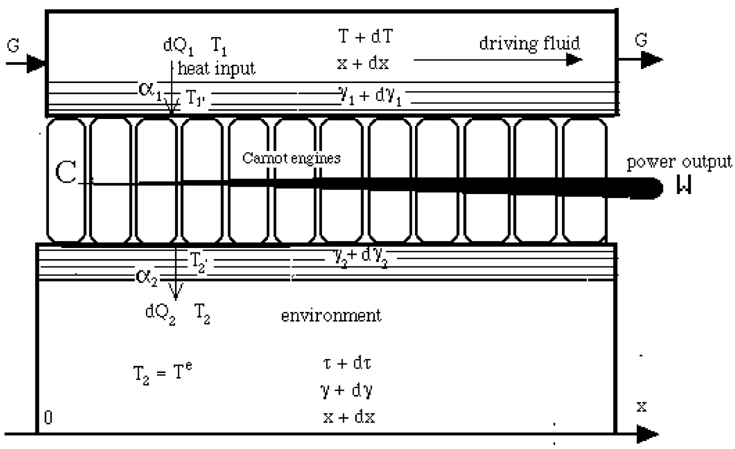

Fig. 1. Model of power production and generalized exergy in an infinite sequence of infinitesimal engines

Modelling a general work-assisted operation for the purpose of limits evaluation is a difficult task as it involves abstract (often 'endoreversible') models and their extensions rather than models of real operations, yet it is consistent with the general philosophy of optimization [53]. Formal analogies do exist between entropy production expressions in work-assisted and in conventional operations that are helpful to develop suitable criteria and models. To develop a quantitative approach to energy limits, we consider the heat transfer-driven work generation (consumption) in an 'endoreversible' thermal machine, an engine or heat pump, which interacts with a high-T fluid (e.g. drying gas) flowing with the mass flux G_f [3], [49], [50]. The finiteness of resources during production (consumption) of work requires the use of the sequence of stages, *Fig. 1*. To get physical rather than economic limits all stages are those with NOVIKOV–CURZON–AHLBORN (NCA) process [49]–[52]; the limits are those for the mechanical or electrical energy. In an endoreversible engine a resource fluid drives the Carnot engine from which the work is taken out. In an endoreversible heat pump a fluid (e.g. drying agent) is driven in the condenser of the Carnot heat pump to which work is supplied; in both cases the second fluid is an infinite reservoir. When real thermal machines are used, endoreversibility assumption can be relaxed. The fluids are of finite thermal conductivity, hence there are finite thermal resistances in the system [3]. In a multistage heating operation the fluid's temperature increases at each stage; the whole operation is described by the sequence $T^0, T^1, \ldots T^N$. The popular 'engine convention' is used: work generated in an engine, W, is positive, and work generated in a heat pump is negative. The state space and its influence on the system dynamics is determined by both the state of the finite-resource fluid flowing through stages of the cascade and the properties of heat bath or the thermal reservoir. In the considered case of an infinite reservoir, the intensive parameters of the reservoir, i.e. its temperature T^e and chemical potentials μ_i^e, do not change along the process path, and this is why these variables reside in the mathematical model as constant parameters only. Thus, it is the condition of an infinite reservoir that enables us to treat the power functions as the reservoir-history independent. Of special attention are two processes: the one which starts with the state $T^0 = T^e$ and terminates at an arbitrary $T^N = T$ and the one which starts at an arbitrary $T^0 = T$ and terminates at T^e. In these cases the optimal functions are generalisation of the classical exergy in discrete processes with finite durations.

Our use of optimization methods in sequential systems with work producers or consumers could, perhaps, make an impression that the goal here is the best economics in thermal machines and/or thermal networks. Should such optimization be the case, a thermal system could be optimized via a customary approach which would require: a detailed network modeling, inclusion of economic accounting, and occasional imbedding of the optimized system into a broader environment to include interacting chains. In fact, the range of optimization in this paper is restricted to thermodynamic limits exclusively, or, as explained above, to a generalized quantity of the exergy type attributed to a definite single stream of substance or energy. Thus we search for the extremum work associated with a finite-time production (consumption) of a single resource stream from (by) the common constituents of environment when this environment is the only source of heat. This exergylike quantity constitutes a generalized potential of extremum work that depends on the end states of the stream and its holdup time in the system (duration). The two sorts of optimization, discussed above, are totally different and any link between them, if at all exists, is indirect at most. To stress these differences, *Figs.2* and *3* compare the scheme of a drying process with endoreversible heat pump with a scheme of a real drying process with a heat pump.

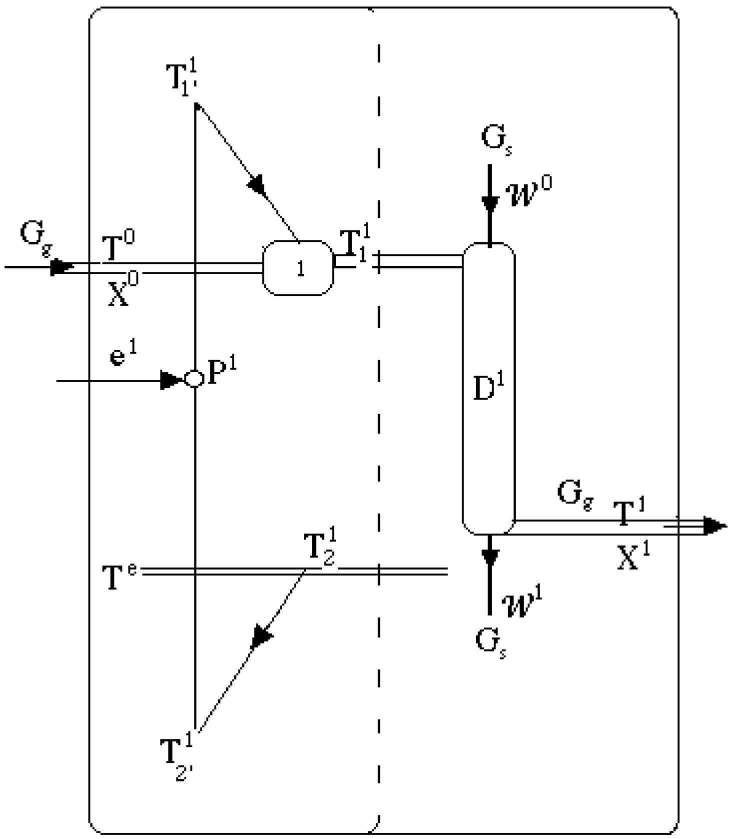

Fig. 2. A scheme of a one-stage drying process with an endoreversible heat pump

In the 'endoreversible' case the perfect efficiency of each Carnot engine contacting with a finite-resource stream is essential, in more general cases, for which the NCA efficiency formula is generalized, internal irreversibilities are included. Work limits follow in terms of the time of state change and properties of boundary layers and other dissipators. The sole dissipation in boundary layers refers to 'endoreversibility' associated with the simplest models of FTT [54]. That modelling is of a very restricted use in predicting actual work characteristics of real thermal machines. Yet, while sufficient to get enhanced limits, the restriction to external irreversibilities is unnecessary, and FTT models can go beyond 'endoreversible

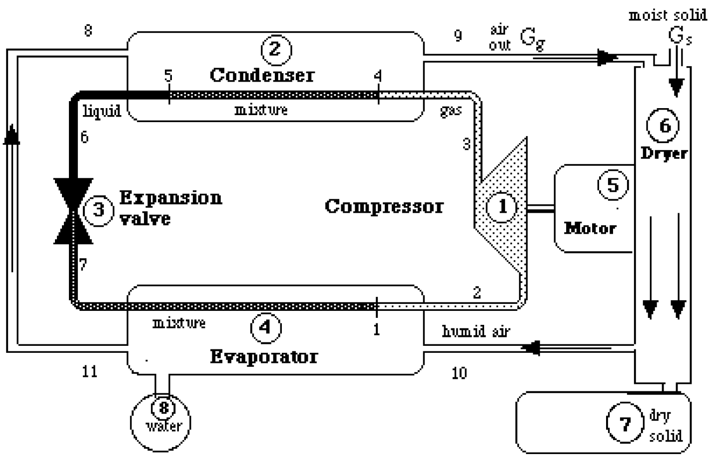

Fig. 3. A scheme of a real drying process with a heat pump

limits' to treat internal irreversibilities as well, see *Eq.* (59) below and [73]. It is most essential, however, that in either of the two methodological versions of FTT, of which the first gives up internal irreversibilities whereas the second one estimates these from a model, the FTT limits on energy consumption or production are stronger than those predicted by the classical exergy. In short, this results from the 'process rate penalty' in every version of FTT. In the hierarchy of limits resulting from more and more detailed models, the limits of the second and higher rank are, of course, stronger than the limits of the first rank (endoreversible limits). The weakest or the worst are limits of classical thermodynamics, resulting from the classical exergy; for the latter function see [46]. Clearly, for the purpose of a real-system optimization, an endoreversible model would be rather insufficient, or even irrelevant get models associated with limits of higher rank can be usable. When calculating energy limits, we search for (hierarchy of) diverse, *purely physical* bounds with no regard to economic optima.

4. Constrained Controls Optimizing Limiting Operations with Heat Transfer

Consider, for example, a single-stage engine process in the standard NOVIKOV–CURZON–AHLBORN operation (NCA engine) in which c is the resource's specific heat, and g_1 and g_2 are thermal conductances [3]. Here we focus on a relatively unknown formulation in which the power of the engine is maximized with respect to both temperatures of the circulating fluid, $T_{1'}$ and $T_{2'}$, that are constrained controls. The constraint is the entropy balance across the engine; the constraining equation is handled by the method of the Lagrange multipliers. This is the formulation where the engine power is expressed by an equation

$$P = g_1 \left(T_1 - T_1'\right) \left(1 - \frac{T_2'}{T_1'}\right). \tag{1}$$

It describes the product of the driving heat and endoreversible efficiency. *Eq.* (1) can be obtained form the original criterion describing power as difference of heat fluxes, $P = q_1 - q_2$, after the second flux, q_2, is eliminated with the help of the entropy balance constraint

$$g_1 \left(T_1 - T_1'\right) / T_1' = g_2 \left(T_2' - T_2\right) / T_2'. \tag{2}$$

The constraint is used here in the form of the continuity of entropy flux. But, since the constraint (2) was already applied, the question arises whether *Eq.* (2) should still be adjoined to (1) in the power optimization procedure using the Lagrange multiplier technique. The valid answer is affirmative; it is substantiated by the argument that only the second flux, q_2, was eliminated, any of two decisions, $T_{1'}$ or $T_{2'}$, are still present in (1). The modified optimization criterion that adjoins the constraint (2) by the Lagrange multiplier λ has the form

$$P' = P + \lambda \cdot C = g_1 \left(T_1 - T_1'\right) \left(1 - \frac{T_2'}{T_1'}\right) + \lambda \left[\frac{g_1 \left(T_1 - T_1'\right)}{T_1'} - \frac{g_2 \left(T_2' - T_2\right)}{T_2'}\right]. \tag{3}$$

Now, for the modified criterion P', coordinates of the stationary point with respect to $T_{1'}$, $T_{2'}$ and λ are determined. This is equivalent to setting to zero respective partial derivatives of the function P'

$$\left(P'\right)_{T_1'} = 0, \quad \left(P'\right)_{T_2'} = 0, \quad \left(P'\right)_{\lambda} = 0. \tag{4}$$

Explicitly, the following set of equations should be solved

$$\begin{aligned}\left(P'\right)_{T_1'} &= -g_1 + g_1 \frac{T_2' T_1}{\left(T_1'\right)^2} - \lambda g_1 \frac{T_1}{\left(T_1'\right)^2} = -g_1 \left(1 + \lambda \frac{T_1}{\left(T_1'\right)^2}\right) \\ &\quad + g_1 \frac{T_2' T_1}{\left(T_1'\right)^2} = 0,\end{aligned} \tag{5}$$

$$\begin{aligned}\left(P''\right)_{T_2'} &= -\frac{g_1 \left(T_1 - T_1'\right)}{T_1'} - \lambda g_2 \frac{T_2}{\left(T_2'\right)^2} = -\frac{g_2 \left(T_2' - T_2\right)}{T_2'} \\ &\quad - \lambda g_2 \frac{T_2}{\left(T_2'\right)^2} = 0,\end{aligned} \tag{6}$$

$$\left(P'\right)_{\lambda} = \frac{g_1 \left(T_1 - T_1'\right)}{T_1'} - \frac{g_2 \left(T_2' - T_2\right)}{T_2'} = 0. \tag{7}$$

Of course, the last equation is the recovered entropy constraint as the extremum condition of P' with respect to λ. The solution of the two previous equations with respect to λ leads respectively to the relations

$$\lambda = T_2' - \frac{\left(T_1'\right)^2}{T_1}, \tag{8}$$

$$\lambda = -T_2' \frac{\left(T_2' - T_2\right)}{T_2} = T_2' - \frac{(T_2')^2}{T_2}. \tag{9}$$

It should be stressed, that if the original criterion, $P = q_1 - q_2$, is treated, in which each of the heat fluxes is expressed in terms of the state variables, T_1 and T_2, and controls, $T_{1'}$ and $T_{2'}$, then the extremal Lagrange multipliers are different from those described by *Eqs*. (8) and (9). With *Eqs*. (8) and (9), temperatures of the circulating fluid are linked by an equation

$$\frac{\left(T_2'\right)^2}{T_2} = \frac{\left(T_1'\right)^2}{T_1}. \tag{10}$$

This is a correct formula connecting the optimal temperatures $T_{1'}$ and $T_{2'}$ in terms of the temperatures of heat sources. *Eq*. (10) leads to a simple relation between temperatures of the circulating fluid

$$T_1' = \sqrt{\frac{T_1}{T_2}} T_2'. \tag{11}$$

Substituting the so-expressed temperature $T_{1'}$ into the equation of the entropy balance we obtain

$$g_1 \left(T_1 - \sqrt{\frac{T_1}{T_2}} T_2' \right) \Big/ \left(\sqrt{\frac{T_1}{T_2}} T_2' \right) = \frac{g_2 \left(T_2' - T_2 \right)}{T_2'}, \tag{12}$$

whence, after rearrangements, the temperature $T_{1'}$ follows as

$$T_2' = \frac{g_1 \sqrt{T_1 \cdot T_2} + g_2 T_2}{g_1 + g_2}. \tag{13}$$

Next, with *Eq*. (11), temperature $T_{2'}$ is obtained

$$T_1' = \frac{g_1 \sqrt{T_1 \cdot T_2} + g_2 T_2}{g_1 + g_2} \cdot \sqrt{\frac{T_1}{T_2}} = \frac{g_1 T_1 + g_2 \sqrt{T_1 \cdot T_2}}{g_1 + g_2}. \tag{14}$$

These are optimal controls, or temperatures of the circulating fluid in the engine at maximum power conditions. One can now calculate the heat fluxes q_1 and q_2:

$$\begin{aligned} q_1 &= g_1\left(T_1 - \frac{g_1T_1 + g_2\sqrt{T_1T_2}}{g_1+g_2}\right) = g_1\left(\frac{g_2T_1 - g_2\sqrt{T_1T_2}}{g_1+g_2}\right) \\ &= g\sqrt{T_1}\left(\sqrt{T_1}-\sqrt{T_2}\right), \\ q_2 &= g_2\left(\frac{g_1\sqrt{T_1T_2}+g_2T_2}{g_1+g_2} - T_2\right) = g_2\left(\frac{g_1\sqrt{T_1T_2}-g_1T_2}{g_1+g_2}\right) = \\ &= g\sqrt{T_2}\left(\sqrt{T_1}-\sqrt{T_2}\right). \end{aligned} \tag{15}$$

In these equations the overall conductance g is defined as the harmonic mean

$$g = \frac{g_1g_2}{g_1+g_2}. \tag{16}$$

The maximum power of the engine system is:

$$\begin{aligned} P &= g\sqrt{T_1}\left(\sqrt{T_1}-\sqrt{T_2}\right) - g\sqrt{T_2}\left(\sqrt{T_1}-\sqrt{T_2}\right) \\ &= g\left(\sqrt{T_1}-\sqrt{T_2}\right)\left(\sqrt{T_1}-\sqrt{T_2}\right) = g\left(\sqrt{T_1}-\sqrt{T_2}\right)^2. \end{aligned} \tag{17}$$

The optimal efficiency of the energy production equals $\eta = 1 - q_2/q_1$, thus, from *Eqs*. (14) and (15)

$$\eta = 1 - \sqrt{T_2/T_1}. \tag{18}$$

While this result is well known, it was obtained in the original paper [16] with a method based on the elimination of variables; its original derivation was therefore much longer.

5. Calculation of Maximum Power for Carnot Temperatures as Optimizing Variables

The traditional overall conductance g governing two-temperature differences as in the case of traditional heat exchange emerges in models of linear power production provided that specific controls are applied in these models, the so-called Carnot temperatures, T' and T''. These temperatures ensure Carnot structure of efficiency equations in irreversible operations. Several details of this approach are described below [50].

The efficiency of thermal engines with irreversible processes is always lower than the Carnot efficiency, $\eta = 1 - T_2/T_1$. From the formal viewpoint, the efficiency lowering may be interpreted in the following way: in order to obtain the correct efficiency of an 'irreversible machine' for a fixed temperature T_2, one should apply in the Carnot formula certain temperature T', lower than the temperature of the fluid bulk, T_1. Let us then introduce such controlling temperature T' for which the efficiency of irreversible operation (consuming or producing work) is expressed by the Carnot formula

$$\eta = 1 - \frac{T_2}{T'}. \tag{19}$$

T' is called the first Carnot temperature, which means that it replaces in an effective way the temperature of the first fluid, T_1. Let us compare expressions for the engine efficiency by using temperatures of the circulating medium $T_{1'}$ and $T_{2'}$ and (first) Carnot temperature T':

$$1 - \frac{T_2'}{T_1'} = 1 - \frac{T_2}{T'}. \tag{20}$$

Evaluation of $T_{2'}$ yields

$$T_2' = \frac{T_2 T_1'}{T'}. \tag{21}$$

We now eliminate with the help of *Eq.* (21) one of the temperatures of the circulating fluid $T_{1'}$ or $T_{2'}$ from the entropy balance. Doing this, for example, with themperature $T_{2'}$ we substitute *Eq.* (21) into (2) to obtain

$$\frac{g_1 \left(T_1 - T_1'\right)}{T_1'} = \frac{g_2 \left(T_2 T_1'/T' - T_2\right)}{T_2 T_1'/T'} \tag{22}$$

or

$$g_1 \left(T_1/T_1' - 1\right) = g_2 \left(1 - T'/T_1'\right). \tag{23}$$

Whence an expression follows that describes $T_{1'}$ in the form

$$T_1' = \frac{g_1 T_1 + g_2 T'}{g_1 + g_2}. \tag{24}$$

Consequently, the heat flux q_1 satisfies an equation

$$q_1 \equiv g_1 \left(T_1 - T_1'\right) = g_1 \left(T_1 - \frac{g_1 T_1 + g_2 T'}{g_1 + g_2}\right) = \frac{g_1 g_2 (T_1 - T')}{g_1 + g_2} = g(T_1 - T'). \tag{25}$$

This means that flux q_1 satisfies the usual expression of Newtonian heat exchange for the overall kinetics (operating with the conductance g) that takes place between two bodies having T_1 and T'.

In processes with heat exchange the single quantity T' is sufficient as independent decision variable. This property follows from the constraint of the balance of entropy, linking $T_{1'}$ and $T_{2'}$. Yet, if one wants to obtain an analogous formula for the second fluid, the second Carnot temperature must be introduced. It is coupled with the temperature T_2 and – by assumption – ensures the efficiency expression in the form

$$\eta = 1 - \frac{T''}{T_1}. \tag{26}$$

Thus the following equation should be satisfied

$$1 - \frac{T_2'}{T_1'} = 1 - \frac{T''}{T_1}. \tag{27}$$

We calculate from this equation $T_{1'}$:

$$T_1' = \frac{T_1 T_2'}{T''}, \tag{28}$$

and substitute it to the entropy balance expressed in terms of temperatures of the circulating medium, $T_{1'}$ and $T_{2'}$. We obtain

$$g_1 \left(T''/T_2' - 1 \right) = g_2 \left(1 - T_2/T_2' \right), \tag{29}$$

whence an equation follows that describes $T_{2'}$ in the form

$$T_2' = \frac{g_1 T'' + g_2 T_2}{g_1 + g_2}, \tag{30}$$

and the heat exchanged with the second reservoir is

$$q_2 \equiv g_2 \left(T_2' - T_2 \right) = g_2 \left(\frac{g_1 T'' + g_2 T_2}{g_1 + g_2} - T_2 \right) = \frac{g_1 g_2 (T'' - T_2)}{g_1 + g_2} = g(T'' - T_2). \tag{31}$$

Comparison of *Eqs.* (20) and (27) yields the following relations that link both Carnot temperatures

$$\frac{T_2'}{T_1'} = \frac{T_2}{T'} = \frac{T''}{T_1}, \tag{32}$$

or

$$T_1 T_2 = T' T''. \tag{33}$$

As these relationships have purely thermodynamic character, they are valid regardless of the mechanism of the heat exchange. In particular, if one admits relations between T' and T_2 or T'' and T_1, these equations are valid for engines working with the exchange of energy of solar radiation. On the other hand, forms of the kinetic *Eqs.* (25) and (31) are constrained to fluids with Newtonian heat exchange.

Summing up we conclude the following. By comparing entropy production expressed in terms of the traditional variables (T_1' and T_2') and in terms of the Carnot variables (T' and T'') we ensured the satisfaction of the classical Carnot formula for the efficiency of irreversible engine in the form $\eta = 1 - T_2/T'$ or in the form

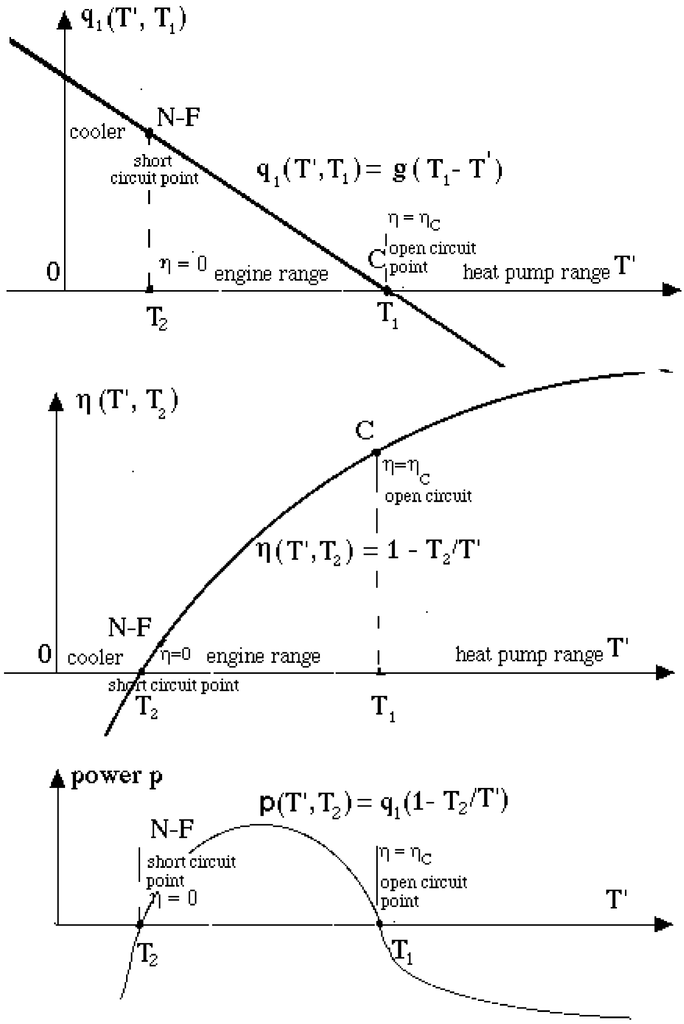

Fig. 4. In terms of the Carnot control T' classical thermodynamic relations and formulas for processes without work are extended to irreversible processes with work production or consumption

$\eta = 1 - T''/T_1$. The comparison of both expressions for η yields the relation $T_1T_2 = T'T''$, which is the suitable constraint condition. General properties of Carnot controls are illustrated in *Figs.* 3 and 4.

We shall now discuss the problems of power optimization with the use of Carnot temperatures as decision variables. As previously, the constraint is repre-

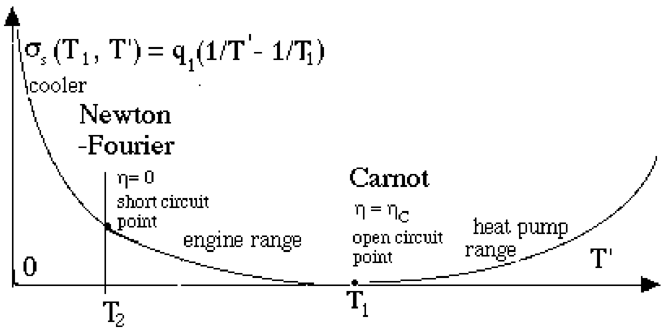

Fig. 5. In terms of the Carnot control T' classical thermodynamic expressions and diagrams for the entropy production in processes without work are extended to processes with work production or consumption

sented by the entropy balance (2′) which, however, must be written down in terms of Carnot variables, T' and T''. The power P expressed in terms of the first and the second Carnot temperatures is

$$P = q_1 - q_2 = g(T_1 + T_2 - T' - T''). \tag{34}$$

Provided that each flux is expressed in terms of its own Carnot temperature, the significance of T' and T'' follows from the observation that in linear systems with power production each expression for heat flux (q_1 or q_2) preserves the traditional (Newtonian) heat exchange. The substantiation for the Newtonian structure of expressions for heats q_1 and q_2, which contain the overall conductance g, was first found in the earlier work [50].

We note that the constraint (33) may also be derived from the condition of the continuity of entropy flux across the engine. The analysis proceeds as follows. We first apply both Carnot temperatures in a form of the entropy balance

$$\frac{g\left(T_1 - T'\right)}{T_1'} = \frac{g\left(T'' - T_2\right)}{T_2'}. \tag{35}$$

Next, we eliminate from this balance one of the remaining temperatures of the circulating fluid, $T_{1'}$ or $T_{2'}$. For this purpose we first compare expression (20) for the engine efficiency in terms of these temperatures and (first) Carnot temperature, T', and then calculate $T_{2'}$ in the form $T_2' = T_2 \cdot T_1'/T$. We substitute this result into the entropy balance, *Eq*. (35). After simplification we obtain the discussed simple constraint (33). The constraint is thus the form expressing the entropy balance in terms of the Carnot variables.

We can now pass to the optimization procedure. The modified optimization criterion has the form

$$P' = P + \lambda \cdot O = g\left(T_1 + T_2 - T' - T''\right) + \lambda\left(T_1 T_2 - T'T''\right). \tag{36}$$

We calculate partial derivatives of the function P' with respect to the Carnot temperatures:

$$\left(P'\right)_{T'} = -g + \lambda\left(-T''\right) = -\left(g + \lambda T''\right), \tag{37}$$
$$\left(P'\right)_{T''} = -g + \lambda\left(-T'\right) = -\left(g + \lambda T'\right). \tag{38}$$

The necessary condition for extremum

$$\left(P'\right)_{T'} = \left(P'\right)_{T''} = \left(P'\right)_{\lambda} = 0 \tag{39}$$

yields the following system of three equations with unknowns λ, T' and T'':

$$g + \lambda T'' = 0, \tag{40}$$
$$g + \lambda T' = 0, \tag{41}$$
$$T_1 T_2 = T' T''. \tag{42}$$

From the first and the second equation, the maximum power condition follows in the form

$$T' = T''. \tag{43}$$

Thus, for the linear NCA engine at the maximum power point both Carnot temperatures are equal. Substituting (43) into the entropy constraint one can evaluate optimal T' and T'':

$$\left(T'\right)^2 = T_1 T_2, \tag{44}$$
$$T' = \sqrt{T_1 T_2}, \tag{45}$$
$$T'' = T' = \sqrt{T_1 T_2}. \tag{46}$$

The optimal efficiency follows then as $\eta = 1 - T_2/T' = 1 - T_2/\sqrt{T_1 T_2}$; thus *Eq.* (18) is valid. This is a well-known result, which was also found previously. The maximum power reads

$$P = g\left(T_1 + T_2 - \sqrt{T_1 T_2} - \sqrt{T_1 T_2}\right)$$
$$= g\left(T_1 + T_2 - 2\sqrt{T_1 T_2}\right) = g\left(\sqrt{T_1} - \sqrt{T_2}\right)^2. \tag{47}$$

All these results conform to those obtained by other methods. Yet, the approach based on the Carnot temperatures has an essential virtue that makes it superior with respect to other approaches. Namely, its basic property is the common analytical formalism that comprises processes in traditional exchangers and work-assisted exchangers. In particular, common for both sorts of operations are analytical expressions describing losses of maximum work and entropy production. In terms of Carnot variables the theory of traditional exchangers is a particular case of the theory of work-assisted operations.

6. Modelling and Evaluation of Extremum Power in Multistage Systems

In this section we use Carnot variables to analyse more complex systems with work flux. To illustrate suitable applications we begin with a single NCA engine with driving fluid at flow or a heat pump with fluid's heat content utilisation [3]. Next we pass quickly to multistage sequential operations. The utilized heat flux which leaves the operation equals $q_1 = -G_f c(T - T^0)$, where G_f is the fluid flow and c is the fluid's specific heat. *Fig. 2* depicts the application of the operation to (say) drying with an endoreversible heat pump, whereas *Fig. 3* refers to a real operation of drying with a heat pump. The specific work produced in a single endoreversible engine or that consumed in a single endoreversible heat pump is [49], [50].

$$W \equiv -p^1/G_f = \left(1 - \frac{T^e}{T'}\right) \frac{g\,(T - T')}{G_f}, \tag{48}$$

where the bracketed expression is the first-law efficiency. Here T', superscripted by n, is the Carnot temperature at stage n, p is the power output, g is an overall thermal conductance of thermal machine related to an overall heat transfer coefficient, α'.

In sequential multistage systems one should sum expressions such as *Eq.* (48) over stages. To cast the problem in the format of the discrete maximum principle we formulate a discrete functional of consumed work

$$\left(-W^N\right) = \sum_{n=1}^{N} c\left(1 - \frac{T^e}{T'^n}\right)\left(T'^n - T^n\right)\theta^n, \tag{49}$$

where $T'^n - T^n = u^n = -q_1^n/g^n$ and $\theta^n = \tau^n - \tau^{n-1}$ is the free increment of nondimensional time τ at stage n. The time itself is defined by *Eq.* (52) below. To obtain the lower endoreversible bound for the consumed work (but not an economic optimum) the specific work (49) has to be minimized subject to the difference constraints

$$\frac{T^n - T^{n-1}}{\tau^n - \tau^{n-1}} = T'^n - T^n; \qquad \frac{\tau^n - \tau^{n-1}}{\theta^n} = 1. \tag{50}$$

The reader should note that the minimum work associated with this energy utilization is a purely physical quantity, i.e. no economic terms are necessary to define the work limit. Leaving aside the finite duration constraint, this is similar to the case of Linde operation, where one evaluates a minimum work of air condensation per unit mass. This is also similar to the evaluation of the classical exergy [46], but is strongly dissimilar to the calculation of the cumulative exergy cost [2], [39], [41] that is influenced by unphysical terms and, therefore, is neither an objective quantity nor an energy limit. *Eq.* (49) describes the work supplied to the operation in which the fluid is sequentially heated in condensers of N endoreversible heat pumps. Yet, the formulation is valid for both process modes, i.e. it includes engines as well. In the limiting case of operation with an infinite number of stages a work integral is obtained in the form of *Eq.* (51). The integral applies the Carnot control $T' = T + u$, where $u = \mathrm{d}T/\mathrm{d}\tau$ holds for the temperature representation of the heat q_1 per unit overall conductance,

$$W \equiv P/G_f = -\int_{T^i}^{T^f} c\left(1 - \frac{T^e}{T}\right)\mathrm{d}T - T^e \int_{T^i}^{T^f} c\frac{\left(T' - T\right)^2}{TT'}\mathrm{d}\tau. \tag{51}$$

Eq. (51) proves that it is the entropy production that causes the non-potential component of the work integral. It refers to a continuous process in which the fluid changes its states between initial temperature T^i and final temperature T^f. The first term is the reversible work W^{rev} (the classical exergy change). The second term is the negative of the ambient temperature and the entropy production. The temperature derivatives and slope coefficients are with respect to the nondimensional time or the number of heat transfer units, τ. The latter can be linked with the length coordinate, x, or the fluid's residence time t

$$\tau \equiv \frac{\alpha' a_v F}{Gc}x = \frac{\alpha' a_v}{\rho c}t = \frac{t}{\chi}, \tag{52}$$

where α' is the overall heat transfer coefficient, a_v – the specific area, F – cross-sectional area for the fluid's flow and $\chi = \rho c/(\alpha' a_v)$ plays the role of a time constant for the system.

As the first or potential term in *Eq.* (51) is path independent, the (nonpotential) entropy production determines the property of the extremal trajectory. A common differential equation holds for extremals of extremum work and minimum entropy production [51]

$$T\frac{\mathrm{d}^2 T}{\mathrm{d}\tau^2} - \left(\frac{\mathrm{d}T}{\mathrm{d}\tau}\right)^2 = 0. \tag{53}$$

Eq. (53) is satisfied by the function $T(t)$ which solves a simple differential equation,

$$\mathrm{d}T/\mathrm{d}\tau = \xi T, \tag{54}$$

where the constant ξ is the rate indicator which is positive for the the fluid's heating and negative for the fluid's cooling. An unconstrained extremal is an exponential curve.

Now we pass to extremals of the underlying multistage process, *Eqs.* (49)–(50). Since the discrete model is linear with respect to the size interval θ^n, a discrete algorithm with a constant Hamiltonian governs the optimal process [52], [53]. The optimal dynamics

$$\frac{T^n - T^{n-1}}{\theta^n} = \xi T^n \tag{55}$$

is a discrete analog of *Eq.* (55). The optimal solution asserts that $\theta^n = \theta^{n-1}$ and

$$\left(T^n\right)^2 = T^{n-1}T^{n+1}. \tag{56}$$

This means that temperatures T^n between the stages n and $n+1$ are geometric means of the boundary temperatures. The discrete solution converges to the exponential solution of *Eq.* (7) in the limit of an infinite N. In fact, *Eq.* (56) is a discrete generalisation of the optimality condition known for optimal trajectories of heat exchangers and simulated annealing [54]–[56]. For exergy boundary conditions, the optimal work associated with *Eq.* (56) is a discrete generalization of the continuous finite-time exergy [51].

7. Unification of Thermal Operations With and Without Work

In terms of the Carnot temperature, or the driving control T', the limiting minimum work in the heat-pump mode can be described by the optimal performance function

$$R\left(T^i, T^f, \tau^f - \tau^i\right) \equiv \min(-P/G_f) = \min \int_{\tau^i}^{\tau^f} c\left(1 - \frac{T^e}{T'}\right)\left(T' - T\right)\,\mathrm{d}\tau$$

$$= h\left(T^f\right) - h\left(T^i\right) - T^e\left(s\left(T^f\right) - s\left(T^i\right)\right) + T^e \min \int_{T^i}^{T^f} c\frac{\left(T' - T\right)^2}{T'T}\mathrm{d}\tau. \quad (57)$$

This refers to the ‘endoreversible’ limit, but it may easily be generalized to processes with internal dissipation as shown below. Likewise, the maximum work in the engine mode is described by the optimal function $V = -R$. In both cases T and T' satisfy the dynamics

$$\mathrm{d}T/\mathrm{d}\tau = T' - T. \quad (58)$$

For multistage processes with heat pumps or engines a fully analogous discrete picture exists with sums replacing integrals and differential ratios instead of derivatives. The discrete counterpart of optimal cost function (57) is then the minimum of expression (49).

Eq. (57) is the endoreversible limit for the work consumption between two given states and for a given number of transfer units. Even this simple limit is stronger than the one predicted by the classical exergy. What can be said about a yet stronger limit which involves an internal dissipation in the participating thermal machine? We need to recall the hierarchy of limits stressed in the Introduction. For limits of higher rank, an internal entropy generation characterised by a parameter p is included in the dissipation model and then *Eq.* (57) is replaced by its simple generalization

$$R\left(T^i, T^f, \tau^f - \tau^i, p\right) = h\left(T^f\right) - h\left(T^i\right) - T^e\left(s\left(T^f\right) - s\left(T^i\right)\right)$$
$$+T^e \min\left(S_\sigma^{\mathrm{int}} + \int_{T^i}^{T^f} c\frac{\left(T' - T\right)^2}{T'T}\mathrm{d}\tau\right). \quad (59)$$

This is in complete agreement with the Gouy-Stodola law. For a still stronger limit, other components of total entropy source are included at the expense of more detailed input of information, but with the advantage that the limit is closer to reality. For a sufficiently high rank of the limit, it approaches the real work quite closely, but also the cost of the related information becomes very large. Hence a proper compromise is essential associated with the accepted limit of a finite rank. For limits of various ranks, inequalities related to R and real work W^{real} are valid in the form $W^{\mathrm{real}} > R^k \ldots > R^1 > R^0$, where R^1 refers to the change of the 'endoreversible exergy', and R^0 – to the change of the classical exergy. The classical exergy change constitutes then the weakest or the worst limit on the real work. In the described scheme any consideration of relation between the irreversibility and costs is unnecessary.

Let us observe that in terms of Carnot control T' the analytical forms of expressions for the entropy production and for the associated dynamics (e.g. *Eq.* (58)) are precisely those which describe a number of purely dissipative processes i.e. those without work production or consumption. For example, with $\tau = G_g c_g/(G_S c_S)$, *Eq.* (58) describes the temperature change of a solid as a controlled phase in the process where gas crosses vertically the bed of the granular solid in a horizontal heat exchanger (HFE). In the process model the equilibrium between the outlet gas and the outlet solid is attained. The integral in the second line of *Eq.* (57) with $c = c_S$ describes the associated entropy production per unit mass of the controlled solid. Indeed, for the 'workless' HFE process we find

$$
\begin{aligned}
S_\sigma &= \int_{T^i}^{T^f} \left(\frac{1}{T} - \frac{1}{T'}\right) \mathrm{d}Q_s = \int_{T^i}^{T^f} c_g \left(\frac{1}{T} - \frac{1}{T'}\right) \left(T' - T\right) \mathrm{d}G_g/G_s \\
&= \int_{T^i}^{T^f} c_s \frac{\left(T' - T\right)}{T'T} \mathrm{d}\tau .
\end{aligned}
\tag{60}
$$

In this case the purely dissipative process of fluidized heat exchange mimics the more difficult process with the endoreversible energy production. The same conclusion holds for cascades with finite number of stages. Such analogies are formal but, nonetheless, they help significantly to optimize work-assisted operations in the realm of the entropy production expressions, not work expressions (work terms are absent in equations of purely dissipative systems). The results found for a horizontal fluidized heat exchanger can be extended to HFE mass exchangers. These continuous systems are limiting configurations for related cascades. Counterparts of resulting expressions for these cascades are derived in a straightforward way: integrals are replaced by corresponding sums.

8. Unified Scheme for Operations of Coupled Heat and Mass Transfer

Here we shall show that operations in conventional HFE dryers can model work-assisted operations with heat and mass transfer. For these processes the controlled phase is solid, and the state space is that of the solid's enthalpy, I, and the solid's moisture content, W. This choice of variables assures the simplest form of the energy and mass balances

$$G_s\,\mathrm{d}I = \mathrm{d}G_g\left(i' - i_s(I,W)\right), \qquad G_s\,\mathrm{d}W = \mathrm{d}G_g\left(X' - X(I,W)\right), \tag{61}$$

where the state of the controlling phase, enthalpy i' and humidity X' is that of the bulk of gas, i.e. $i' = i_g$ and $X' = X_g$. We aim to derive suitable formulae for entropy production or exergy dissipation that will be useful for evaluation of work limits in thermal machines. We assume a complete utilization of the outlet gas.

The specific entropy produced per unit mass of solid is the path integral over the scalar product of vectors $(\mathrm{d}I, \mathrm{d}W)$ and $(1/T - 1/T', \mu/T - \mu'/T')$. The difference of Planck potentials drives the mass transfer. Thus, with energy and mass balances (61)

$$\begin{aligned} S_\sigma &= \int_{T^i}^{T^f} \left(\frac{1}{T} - \frac{1}{T'}\right)\mathrm{d}I - \left(\frac{\mu}{T} - \frac{\mu'}{T'}\right)\mathrm{d}W \\ &= \int_{T^i}^{T^f} \left[\left(\frac{1}{T} - \frac{1}{T'}\right)(i' - i_s) + \left(\frac{\mu'}{T'} - \frac{\mu}{T}\right)(X' - X_s)\right]\mathrm{d}\tau. \end{aligned} \tag{62}$$

With the Hessian of entropy s' of the controlling phase, which is the matrix of the second order derivatives of s' with respect to i' and X', the Taylor expansion of thermodynamic forces up to the second order terms yields a positive integral

$$S_\sigma = \int_{T^i}^{T^f} \left[\left| \begin{matrix} (i' - i_s) \\ (X' - X_s) \end{matrix} \right| \left| \begin{matrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{matrix} \right| \left| \, (i' - i_s) \quad (X' - X_s) \, \right| \right] \mathrm{d}\tau, \tag{63}$$

where the positive matrix $\Gamma_{ik} = -\partial^2 s'/\partial x^i \partial x^k\, \mathrm{d}x^k$ is the negative Hessian of entropy s'. The benefit is the entropy source in an explicit form usable to get endoreversible limits. The quantity S_σ for the multistage process is the corresponding sum. Yet if the Onsager's theory is applied an alternative of *Eq.* (63) is obtained in terms of rates and overall resistances r

$$S_\sigma = \int_{T^i}^{T^f} \left(\frac{1}{T} - \frac{1}{T'}\right) \mathrm{d}I + \left(\frac{\mu'}{T'} - \frac{\mu}{T}\right) \mathrm{d}W$$
$$= \int_{T^i}^{T^f} \left[r^{II}\dot{I}^2 + 2r^{IW}\dot{W}\dot{I} + r^{WW}\dot{W}^2\right] \mathrm{d}\tau. \tag{64}$$

Eqs. (63), (64) and their discrete analogs represent the continuous and discrete generalizations of *Eq.* (60) for mass transfer coupled with transfer of heat. Optimization of criteria of this sort leads quite generally to constancy of S_σ along optimal paths [54]–[56], or to the 'equipartition of the entropy production' first described by TONDEUR and KVAALEN [57]. However, that principle is valid only in the case without constraints imposed on parameters of the controlling phase (gas). Post-quadratic terms in the optimization criterion and nonlinearities in kinetic equations may also cause the violation of the principle.

An expression such as *Eq.* (63) applies also in the realm of thermal machines, as a representation of the endoreversible component of their lost work divided by T^e. The optimization of *Eq.* (63) automatically eliminates the controlling (primed) parameters from S_σ, thus generating the potential R_σ which depends only on the initial and final states of the considered phase and the process duration. However, up to now a precise set of conditions under which *Eq.* (63) could serve as a suitable model for a work-assisted system is unknown. Extended studies in FTT of complex engines and heat pumps with heat and mass transfer are further necessary [58]. In such systems humid gases and hygroscopic solids are utilized by endoreversible heat pumps while exchanging mass and heat. Minimization of the total work consumed in a finite duration leads to finite-time exergies of gas and solid, A_g and A_S. Formulae for such exergies follow from *Eqs.* (49) and (57) when final states are identified with states of equilibrium with the environment [58], [59]. With the knowledge of the classical exergy, A^{rev}, a numerical procedure generates data for both A and min S_σ. A finite-time exergy of a humid gas, A, is found [59] which contains the classical exergy of this gas [46], [47] increased in the case of heat pump mode by the product of the environment temperature T^e and the minimum entropy production, S_σ. For the engine mode, the classical exergy is decreased by the product of the environment temperature T^e and min S_σ. For continuous changes of the gas state $A = A^{\mathrm{rev}} \pm T^e \min S_\sigma$. The plus sign refers to processes departing from the equilibrium and the minus sign to those approaching the equilibrium. The reversible component in A agrees with a general formula for the classical thermal exergy of a non-reacting mixture [46]. For a multistage process, a discrete counterpart of A can be generated numerically; the computations should refer to a sufficiently large N in order to accurately approximate the continuous exergy. For example, with classical exergy of a solid [47] and *Eq.* (62) one can generate numerically the finite-time work potential for the solid. By exploiting the heat and mass transfer analogies [58], we apply *Eq.* (62) as a proper formula to evaluate minimum $S_\sigma = R_\sigma$ in operations with thermal machines.

9. Peculiarities Accompanying Solar-Assisted Operations

The basic idea of the method that uses the Carnot intensity variables is based on the identity of *thermodynamic* equations describing the entropy production in processes with and without work in terms of the control variables T' and μ'. The abstract nature of these equations makes them free from the time variable and materials characteristics. On the other hand identity of *kinetic* expressions holds only for linear kinetic models. In general nonlinear cases the identity is not satisfied; thus the use of control variables T' and μ' requires modification. While the full coincidence is still attained at the 'short circuit point', beyond that point the overall kinetics depends on controls (T' and μ') and the form divergence is observed in the structure of both equations. Our process description must take into account this peculiarity. It is restricted to assure at the Carnot point the satisfaction of the basic equalities: $T' = T_1 = T_{1'}$, $T'' = T_2 = T_{2'}$, $\eta = 1 - T_2/T_1$, $q_1 = q_2 = p = 0$.

An example are equations of the radiative engine, also called the Stefan–Boltzmann engine, where upper and lower heat exchange undergo in accordance with the radiation laws [60]

$$q_1 = g_1(T_1^4 - T_{1'}^4), \tag{65}$$

$$q_2 = g_2(T_{2'}^4 - T_2^4). \tag{66}$$

In spite of the model's simplicity, its two 'resistive parts' take rigorously into account the entropy generation caused by simultaneous emission and absorption of black-body radiation, the model's property which some of FTT adversaries seem not to be aware of [78]. This entropy generation follows as the 'classical' sum: $q_1(T_{1'}^{-1} - T_1^{-1}) + q_2(T_2^{-1} - T_{2'}^{-1})$, where each q_i is given by the Stefan–Boltzmann law, *Eqs.* (65) and (66). Along with the two efficiency expressions we have at our disposal the equality

$$\eta = 1 - T_{2'}/T_{1'} = 1 - T_2/T' \tag{67}$$

whence

$$T_{2'} = T_{1'}T_2/T'. \tag{68}$$

Substituting this expression into the continuity equation for the entropy flux

$$g_1(T_1^4 - T_{1'}^4)/T_{1'} = g_2(T_{2'}^4 - T_2^4)/T_{2'}, \tag{69}$$

we obtain a single equation for $T_{1'}$. Then, after using this $T_{1'}$ and *Eq.* (68) again, we obtain an analogous equation for $T_{2'}$. Next, with Stefan–Boltzmann equations (65) and (66), we calculate heat fluxes, q_1 and q_2. The resulting heat flux q_1 in terms of T' has the form [79]

$$q_1 = g_1 g_2 \frac{T_1^4 - T'^4}{g_1 (T'/T_2)^3 + g_2}. \tag{70}$$

In a similar way an equation is obtained that describes the second heat flux, q_2

$$q_2 = g_1 g_2 \frac{T''^4 - T_2^4}{g_1 + g_2 (T''/T_1)^3}. \tag{71}$$

Note that, correspondingly with $1 - \eta = T_2/T' = T''/T_1$, the heat flux q_1 was expressed in terms of the controlling temperature T' whereas the flux q_2 – by the temperature T''. The equality $T'T'' = T_1 T_2$ was exploited here to get the second Carnot temperature. At the Carnot point the following equalities are satisfied: $T' = T_1 = T_{1'}$, $T'' = T_2 = T_{2'}$, $\eta = 1 - T_2/T_1$, $q_1 = q_2 = p = 0$. Therefore, the heat fluxes expressed by their own control temperatures (T' for q_1 and T'' for q_2) satisfy equations which are similar but not identical with equations of the corresponding process without work. Only at the short circuit point, where $T' = T_2$ and $T'' = T_1$ and $q_1 = q_2$, *Eqs.* (70) and (71) yield

$$q_1 = g[T_1^4 - T'^4] = g[T''^4 - T_2^4]. \tag{72}$$

Clearly *Eqs.* (70) and (71) rather than *Eq.* (72) should be used in evaluating the work limits for solar assisted operations.

10. Energy Limits in Living Systems

The above considerations and analyses can be extended to optimization in systems with living organisms. We focus on energy limits associated with the so-called complexity [61] and information-theoretic models for sequentially evolving states [62]. The information concept is not only appropriate to complex systems but is also quantitatively well defined [63]. Diverse models serve to evaluate energy limits quantitatively [64]. In living systems non-equilibrium entropy has to be applied [65].

Living systems have developed various strategies to manipulate their self-organization in order to satisfy the principle of minimum complexity increase, ultimately, however, the physical laws set limits to their size, functioning and rate of development. For example, the physical law of thermal conduction sets the size of warm-blooded aquatic animals that require a minimum diameter (of ca. 15 cm) in order to survive in cold oceans [66]. Species that survive in ecosystems are those that funnel energy into their own production and reproduction and contribute to autocatalytic processes in the ecosystem. Also, there are data that show that poorly developed ecosystems degrade the incoming solar energy less effectively than more mature ecosystems [67]. The cornerstone here is to view living systems as stable structures increasing the degradation of the incoming solar energy, while surviving in a changing and sometimes impredictable environment. All these structures have one feature in common: they increase the system's ability to dissipate the applied gradient in accordance with the so-reformulated second law of thermodynamics [67]. In all these situations the second law imposes constraints that are necessary but not sufficient cause for life itself. Reexamination of thermodynamics proves that the second law underlines and determines the direction of many processes of the development of living systems. As an ecosystem develops it becomes more effective in removing the exergy part in the energy it captures, and this exergy is utilized to build and support organization and structure. Time and its derivative cycling play a key role in the evolution.

Optimization of pulsating physiological processes can shed light on the basic understanding of development and evolution [68]. Optimal strategies of streets tree networks and urban growth can mimic the development of living systems [69]. Information theory helps to display the thermodynamic behavior of living systems during their development and evolution [70]. Living organisms are treated therein as multistage systems by a complexity criterion based on information-theoretic entropy. Some features of living organisms can be predicted when describing their evolution in terms of extremum principles for shortest paths along with suitable transversality conditions. In their models quantities similar to entropy production are extremized, and Onsager-like symmetries are found in models of development [62]. Discrete and nonlinear models are suitable to describe dynamics in metric spaces.

11. Final Remarks

First of all we stress the observation that even the non-Newtonian nature of heat and/or mass transfer (when described in terms of Carnot intensities or primed quantities) does not change the general thermodynamic formalism. On the other hand, the non-Newtonian nature influences the formal structure of the heat and mass exchange equations only beyond their linear approximation. Since various industrial bodies may exhibit complex non-Newtonian properties, the method is capable of evaluating energy limits in arbitrarily complex mass transfer and heating systems (with, e.g., drying bodies, radiation fluids, polymers, etc.). This is a fundamental point, which is also the feature that makes our results essential. In fact, it is the complexity of rheological properties of substances used in industry and practical devices which makes our general results valuable in diverse operations.

Sometimes a scepticism is expressed whether the principles based on finite time thermodynamics can be useful to optimize thermal systems with non-equilibrium processes, especially systems of complex topology such as thermal networks [71], [72], [78]. While a large portion of these objections can be overcome [73], we shall not enter here into this debate, as it is enough to recall the assertion made in the introduction of this paper. It states that an economic problem of the system optimization and the physical problem of work limits for a resource (considered here) are two different problems. The real work supplied to a compressor at economically optimal conditions may sometimes be dozen times larger than the mechanical energy (exergy) limit required to produce a key substance; this is a well known fact from the theory of Linde operation, for example [31], [74], [79]. For the notion of energy limits, the trade-off between the exploitation and investment costs and the investment reduction by admission of exergy losses are most often irrelevant issues. Yet, at the interface of thermodynamics with economics all such issues are essential [75], [76]. Also, the entropy source minimization, restricted to the physical system, may have no relevance to an economic optimum of a product yield, where some cumulative generation criteria may be attributed to a valuable final product [2], [42]–[46]. On the other hand, these cumulative criteria have little in common with physical limits on energy use.

Our method does yield endoreversible and higher-order generalizations of the standard exergy. At the zero-th rank all processes are reversible, and only then our method yields the standard exergy function. In general, the method serves to evaluate enhanced energy limits in highly non-equilibrium, kinetically driven processes of mass and energy transfer. We stress the hierarchical nature of the FTT limits, where endoreversible limits are one step better than those derived from the classical exergy. In the considered radiation model, the endoreversible step is just the step forward sufficient to incorporate the entropy production caused by simultaneous emission and absorption of radiation. Of the two basic fields compared, exergy analysis and FTT, only the latter can systematically include various concepts of contemporary irreversible thermodynamics. To evaluate energy limits of lowest ranks, FTT acts in a seemingly oversimplified manner: it often cuts the hierarchy of the limits at the level of the endoreversibility (endoreversible exergies), and works often with kinetic models based on ordinary differential equations. The simplicity of these models and an aggregated information on which FTT rests are frequently the source of misunderstanding. Adversaries of FTT commonly ignore the fact that the useful notion of the classical exergy is associated with even more simple models than endoreversible: the reversible ones. In fact, limits of higher ranks refer to more realistic models, and the potential of FTT for incorporating results of dissipative fluid mechanics or nonequilibrium field thermodynamics in an exact way has been shown [30], [77]. The role of FTT should become more pronounced in the future in view of its flexibility in generating irreversible limits of any order with information contained in the entropy generation. Its potential is enhanced by the explicit use of the concept of the process state and state control in the sense of process dynamics.

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Nomenclature

A	available energy (exergy)
b_g, b_s	specific exergy of gas and gas in equilibrium with solid
b'	specific exergy of controlling phase
c	specific heat at the constant pressure
G	mass flux, total flow rate
g_1, g	partial and overall conductances
H_{TU}	heat of transfer unit
I^n	solid's enthalpy at stage n
i'	specific enthalpy of controlling phase
i_g, i_s	specific enthalpy of gas and gas at equilibrium with solid
N	total number of stages in a multistage process
n	current stage number of a multistage process
P^n, p^n	cumulative power output and power output at the n-th stage
q_1	driving heat in the engine mode of the stage
$R^n(x, t)$	optimal work function of cost type in terms of state and time
S	solid's entropy, entropy of controlled phase (solid)
s'	specific entropy of controlling phase (gas)
S_σ	specific entropy production
T	temperature of controlled phase (solid)
T^e	constant equilibrium temperature of reservoir
T'	Carnot temperature, temperature of controlling phase (gas)
t	physical time, contact time
$u^n = \Delta T^n/\Delta\tau^n$	rate of the temperature change as the control variable
$V = \max W$	optimal work function of profit type
$W = P/G$	total specific work or total power per unit mass flux
W^n	moisture content in solid from stage n
X'	absolute humidity of controlling phase (gas)
x	transfer area coordinate

Greek Symbols

α'	overall heat transfer coefficient
$\eta = p/q_1$	first-law efficiency
θ^n	free interval of an independent variable or time interval at stage n
μ_k	molar chemical potential of k-th component
μ'	coefficient of outlet gas utilization
τ	nondimensional time, number of the heat transfer units (x/H_{TU})

Subscripts

g	gas
i	i-th state variable
s	saturation, solid

1, 2	first and second fluid

Superscripts

e	environment, equilibrium
f	final state
i	initial state
k or *n*	number of *k*-th or *n*-th stage

Abbreviations

EGM	entropy generation minimization
FTT	finite time thermodynamics

References

[1] DE VOS, A., *Endoreversible Thermodynamics of Solar Energy Conversion*, Clarendon Press, Oxford (1992), pp. 29–51.

[2] SZARGUT, J., Sequence Method of Determination of Partial Exergy Losses in Thermal Systems, *Exergy Int. J.* **1** (2001), pp. 39–64, See also: SZARGUT, J., Analiza egzergetyczna w energetyce cieplnej, Ekspertyza KTiSp PAN: Wspótczesne Kierunki w Termodynamice, Bilicki, Z., Mikielewicz, J., Sieniutycz, S., (eds.), Wydawnictwa Politechniki Gdańskiej, Gdańsk, 2001.

[3] BERRY, R. S. – KAZAKOV, V. A. – SIENIUTYCZ, S. – SZWAST, Z. – TSIRLIN, A. M., *Thermodynamic Optimization of Finite Time Processes*, Wiley, Chichester 2000. See also: SIENIUTYCZ, S., Nonlinear Dynamics of Generalized Carnot Problem of Maximum Work Received in Finite Time from a System of Two Continua with Different Temperatures, *Periodica Polytechnica, Ser. Chem. Eng.* **42** (1998), pp. 33–54.

[4] SIENIUTYCZ, S., Hamilton-Jacobi-Bellman Framework for Optimal Control in Multistage Energy Systems, *Physics Reports* 326, issue 4, March 2000, pp. 165–285, Elsevier, Amsterdam, 2000.

[5] FAN, L. T., *The Continuous Maximum Principle, A Study of Complex System Optimization*, Wiley, New York, 1966.

[6] ARIS, R., *Discrete Dynamic Programming*, Blaisdell, New York, 1964.

[7] ANDRESEN, B. – GORDON, J., Optimal Paths for Minimizing Entropy Production in a Common Class of Finite-Time Heating and Cooling Processes, *Intern. J. Heat Fluid Flow*, **13** (1992), pp. 294–299.

[8] ANDRESEN, B. – SALAMON, P. – BERRY, R. S., Thermodynamics in Finite Time, *Physics Today*, September 1984, pp. 62–70.

[9] SALAMON, P. – ANDRESEN, B. – BERRY, R. S., Thermodynamics in Finite Time. II. Potentials for Finite-Time Processes, *Phys. Rev. A*, **15** (1977), pp. 2094–2095.

[10] SIENIUTYCZ, S., The Thermodynamic Approach to Fluidized Drying and Moistening Optimization, *A.I.Ch.E. Journal*, **19** (1973), pp. 277–285.

[11] DANTZIG, G. B., *Linear Programming and Extensions*, Princeton University Press, Princeton, 1968.

[12] ZANGWILL, W. I., *Nonlinear Programming*, WNT, Warsaw, 1974.

[13] SIENIUTYCZ, S., *Optimization in Process Engineering*, 2-nd edn., WNT, Warsaw, 1991.

[14] PONTRYAGIN, L. S. – BOLTYANSKI, V. G. – GAMKRELIDZE, R. V. – MISCHENKO, E. F., *The Mathematical Theory of Optimal Processes*, Interscience Publishers, New York, 1962.

[15] LEITMAN, G., *An Introduction to Optimal Control*, McGraw Hill, New York, 1966.

[16] CURZON, F. L. – AHLBORN, B., Efficiency of Carnot Engine at Maximum Power Output, *Amer. J. Phys.*, **43** (1975), pp. 22–24.

[17] HOFFMANN, K. H. – ANDRESEN, B. – SALAMON, P., Measures of Dissipation, *Phys. Rev. A.*, **39** (1989), pp. 3618–3621.

[18] ANDRESEN, B., *Finite-Time Thermodynamics*, University of Copenhagen, Copenhagen, 1983.

[19] BERRY, R. S. – SALAMON, P. – HEAL, G., On the Relation Between Thermodynamic and Economic Optima, *Resources and Energy*, **1** (1978), pp. 125–127.

[20] SZARGUT, J. – PETELA, R., *Exergy*, WNT, Warsaw, 1965.

[21] KOTAS, T. J., *Exergy Method of Thermal Plant Analysis*, Butterworths, Borough Green, 1985.

[22] SZARGUT, J., Application of Exergy in Establishing of Generalized Technical-Economical Interdependences, *Arch. Bud. Maszyn*, **17** (1970), pp. 105–108.

[23] BEJAN, A., The Thermodynamic Design of Heat and Mass Transfer Processes and Devices, Review, *Heat and Fluid Flow*, **8** (1987), pp. 258–276.

[24] GORDON, J. M., Nonequilibrium Thermodynamics for Solar Energy Applications, Article in: *Finite-Time Thermodynamics and Thermoeconomics*, eds. Sieniutycz, S., and P. Salamon, P., *Advances in Thermodynamics*, 4, Taylor and Francis, New York, 1990, pp. 95–120.

[25] ONDRECHEN, M. J. – ANDRESEN, B. – MOZURKEWICH, M. – BERRY, R. S., Maximum Work from a Finite Reservoir by Sequential Carnot Cycles, *Am. J. Phys.*, **49** (1981), pp. 681–684.

[26] GORDON, J. M., Generalized Power Versus Efficiency Characteristics of Heat Engines: The Thermoelectric Generator as an Instructive Illustration, *Am. J. Phys.*, **59** (1991), pp. 551–555.

[27] GORDON, J. M. – HULEIHIL, M., On Optimizing Maximum-Power Heat Engines, *J. Appl. Phys.*, **69** (1991), pp. 1–7.

[28] YAN, Z. – CHEN, J., Optimal Performance of a Generalized Carnot Cycle for another Linear Heat Transfer Law, *J. Chem. Phys.*, **92** (1990), pp. 1994–1998.

[29] CHEN, J. – YAN, Z., Unified Description of Endoreversible Cycles, *Phys. Rev. A*, **39** (1989), pp. 4140–4147.

[30] ORLOV, V. N. – BERRY, R. S., Estimation of Minimal Heat Consumption for Heat-Driven Separation Processes via Methods of Finite-Time Thermodynamics, *J. Phys. Chem.*, **95** (1991), pp. 5624–5628.

[31] CIBOROWSKI, J., *Fundamentals of Chemical Engineering*, WNT, Warsaw, 1965.

[32] BODVARSSON, G. S. – WITHERSPOON, P. A., Geothermal Reservoir Engineering Part 1, *Geothermal Sci. Tech.*, **1** (1989), pp. 1–2.

[33] NEILL, D. T. – JENSEN, W. P., Geothermal Powered Heat Pumps to Produce Process Heat, *Proc. 11 Intersoc. Energy Conversion Engineering Conference*, USA, 1976.

[34] GUSTAVSON, M., Limits to Wind Power Utilization, *Science*, **204** (1979), p. 13.

[35] LANDSBERG, P., Statistics and Thermodynamics of Energy Conversion from Radiation, in: *Nonequilibrium Theory and Extremum Principles, Adv. in Thermodyn. Series*, **3** (1990), pp. 482–536.

[36] JARZEBSKI, Z. M., *Solar Energy Photovoltaic Conversion*, PWN, Warsaw, 1990.

[37] MANSOORI, G. A. – PATEL, V., Thermodynamic Basis for the Choice of Working Fluids for Solar Absorption Cooling Systems, *Solar Energy*, **22** (1979), pp. 483–491.

[38] SZARGUT, J., Minimization of the Consumption of Natural Resources, *Bull. Acad. Pol. Tech.*, **26** (1978), pp. 41–45.

[39] SZARGUT, J., Application of Exergy for Calculation of Ecological Cost, *Bull. Polish Acad. Sci. Tech. Sci.*, **34** (1986), pp. 475–480.

[40] MÅNSSON, B. Å., Thermodynamics and Economics, Article in: *Finite-Time Thermodynamics and Thermoeconomics*, eds. Sieniutycz, S., and P. Salamon, P., *Advances in Thermodynamics*, 4, Taylor and Francis, New York, 1990, pp. 153–174.

[41] SZARGUT, J., Analysis of Cumulative Exergy Consumption and Cumulative Exergy Losses, Article in: *Finite-Time Thermodynamics and Thermoeconomics*, eds. Sieniutycz, S., and P. Salamon, P., *Advances in Thermodynamics*, 4, Taylor and Francis, New York, 1990, pp. 278–302.

[42] SZARGUT, J., Analysis of Cumulative Exergy Consumption, *Intern. J. Energy Research*, **11** (1987), pp. 541–547.

[43] SZARGUT, J. – MORRIS, D. R., Cumulative Exergy Consumption and Cumulative Degree of Perfection of Chemical Processes, *Intern. J. Energy Research*, **11** (1987), pp. 245–261.

[44] SZARGUT, J. – MAJZA, E., Thermodynamic Imperfection and Exergy Losses at Production of Pig Iron and Steel, *Arch. Metallurgy*, **34** (1989), pp. 197–216.

[45] SZARGUT, J., Indices of the Cumulative Consumption of Energy and Exergy, *Zeszyty Nauk. Polit. Slaskiej: Ser. Energetyka*, **106** (1989), pp. 39–55.

[46] SZARGUT, J. – MORRIS, D. R. – STEWARD, F., *Exergy Analysis of Thermal, Chemical and Metallurgical Processes*, Hemisphere, New York, 1988.

[47] SIENIUTYCZ, S., Computing of Thermodynamic Functions in Gas-Moisture-Solid Systems, *Reports of Inst. Chem. Engng., Warsaw Tech. Univ.*, **2** (1973), pp. 323–349.

[48] SIENIUTYCZ, S., Optimal Control in Multistage Flow Systems by Hamilton-Jacobi-Bellman, *Archiv. of Thermodyn.* **20** (1999), pp. 27–48.

[49] SIENIUTYCZ, S. – BERRY, R. S., Discrete Hamiltonian Analysis of Endoreversible Thermal Cascades, Chapter 6 in the book: *Thermodynamics of Energy Conversion and Transport*, eds. S. Sieniutycz and A. de Vos, Springer N.Y., 2000, pp. 143–172.

[50] SIENIUTYCZ, S., Endoreversible Modeling and Optimization of Thermal Machines by Dynamic Programming, Chap. 11 in the book: *Recent Advance in Finite Time Thermodynamics*, ed. Ch. Wu, Nova Science, New York (1999), pp. 189–220.

[51] SIENIUTYCZ, S., Hamilton-Jacobi-Bellman Theory of Irreversible Thermal Exergy, *Intern. J. Heat and Mass Transfer*, **41** (1998) pp. 183–195.

[52] ANDRESEN, B. – RUBIN, M. H. – BERRY, R. S., Availability for Finite-Time Processes. General Theory and Model, *J. Phys. Chem.*, **87** (1983), pp. 2704–2713.

[53] SIENIUTYCZ, S. – SZWAST, Z., *Practice in Optimization*, Wydawnictwa Naukowo Techniczne, Warsaw (1982).

[54] SALAMON, P. – NITZAN, A. – ANDRESEN, B. – BERRY, R. S., Minimum Entropy Production and the Optimization of Heat Engines, *Phys. Rev. A*, **21** (1980), pp. 2115–2129.

[55] ANDRESEN, B. – GORDON, J., Constant Thermodynamic Speed for Minimizing Entropy Production in Thermodynamic Processes and Simulated Annealing, *Phys Rev. E.*, **50** (1994), pp. 4346–4351.

[56] SPIRKL, W. – RIES, H., Optimal Finite-Time Endoreversible Processes, *Phys. Rev. E*, **52** (1995), pp. 3485–3489.

[57] TONDEUR, D. – KVAALEN, E., Equipartition of Entropy Production: an Optimality Criterion for Transfer and Separation Processes, *Ind. Eng. Chem. Research*, **26** (1987), pp. 50–56.

[58] SIENIUTYCZ, S., Optimal Control Framework for Multistage Engines with Heat and Mass Transfer, *J. Non-Equilibrium Thermodyn.*, **24** (1999), pp. 40–74.

[59] SIENIUTYCZ, S., Thermodynamic Optimization for Work-Assisted Heating and Drying Operations, *Energy Conversion & Management*, **41** No. 18 (2000), pp. 2009–2031.

[60] DE VOS, A., The Endoreversible Theory of Solar Energy Conversion: a Tutorial, *Solar Energy Materials and Solar Cells*, **31** (1993), pp. 75–93.

[61] SHINER, J. S. – DAVISON, M. – LANDSBERG, P. T., Simple Measure for Complexity, *Phys. Rev. E.*, **59** (1999), pp. 1459–1464.

[62] SZWAST, Z. – SIENIUTYCZ, S. – SHINER, J. S., Complexity Principle of Extremality in Evolution of Some Living Organisms by Information-Theoretic Entropy, *Chaos, Solitons and Fractals*, **13** (2002), pp. 1871–1888.

[63] SHANNON, C. E. – WEAVER, W., *The Mathematical Theory of Communication*, The University of Illinois Press, Urbana 1969.

[64] AHLBORN, B. K., Thermodynamic Limits of Body Dimension of Warm Blooded Animals, *J. of Non-Equilib. Thermodyn.*, **40** (1999), pp. 407–504.

[65] LANDAU – LIFSHITZ, *Statistical Physics*, Pergamon, Oxford 1975.

[66] AHLBORN, B. K. – BLAKE, R. W., Lower Size Limit of Aquatic Mammals, *Am. J. of Phys.*, **67** (1999), pp. 1–3.

[67] SCHNEIDER, E. – KAY, J., Complexity and Thermodynamics: Towards a New Ecology, *Future*, **26** (1994), pp. 626–647.

[68] BEJAN, A., Theory of Organization in Nature: Pulsating Physiological Processes, *Intern. J. Heat and Mass Transfer*, **40** (1997), pp. 2097–2104.

[69] BEJAN, A. – LEDEZMA, G. A., Streets Tree Networks and Urban Growth: Optimal Geometry for Quickest Access between a Finite-Size Volume and One Point, *Physica A*, **255** (1998), pp. 211–217.

[70] SZWAST, Z., An Approach to the Evolution of Selected Living Organisms by Information-Theoretic Entropy, *Reports of Faculty of Chemical and Process Engineering at Warsaw TU*, **24** (1997), pp. 123–143.

[71] SZARGUT, J., Problems of Thermodynamic Optimization, *Archives of Thermodynamics*, **19** (1998), pp. 85–94.

[72] MORAN, M. J., On Second-Law Analysis and the Failed Promise of Finite-Time Thermodynamics, *Energy*, **6** (1998), pp. 517–519.

[73] CHEN, J. – YAN, Z. – LIN, G. – ANDRESEN, B., On the Curzon-Ahlborn Efficiency and its Connection with the Efficiencies of Real Heat Engines, *Energy Conversion & Management*, **42** (2001), pp. 173–181.

[74] BOSNIAKOVIC, F., *Technische Thermodynamik, I und II*, Theodor Steinkopff, Dresden 1965.

[75] CLARK, J. A., Thermodynamic Optimization, Interface with Economic Analysis, *J. Non-Equilib. Thermodyn.*, **10** (1986), pp. 85–122.

[76] EL-SAYED, Y. M., Thermodynamics and Thermoeconomics, *Int. J. Applied Thermodyn.*, **2** (1999), pp. 5–18.

[77] ORLOV, V. N. – BERRY, R. S., Power Output from an Irreversible Heat Engine with a Nonuniform Working Fluid, *Phys. Rev. A*, **42** (1990), pp. 7230–7235.

[78] SZARGUT, J., Letter to the Editor, *Archives of Thermodynamics*, **22** (2001), pp. 36–37.

[79] SIENIUTYCZ, S., Thermodynamic Optimization for Work-Assisted and Solar-Assisted Heat and Mass Transfer Operations, *Archives of Thermodynamics*, **22** (2001), pp. 17–36.