PERGAMON

International Journal of Heat and Mass Transfer 45 (2002) 2995–3012

International Journal of HEAT and MASS TRANSFER

www.elsevier.com/locate/ijhmt

Dynamical energy limits in traditional and work-driven operations I. Heat-mechanical systems

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Received 4 December 2001

Abstract

Using irreversible thermodynamics we define and analyze dynamic limits for various traditional and work-assisted processes of sequential development with finite rates important in engineering. These dynamic limits are functions rather than numbers; they are expressed in terms of classical exergy change and a residual minimum of dissipated exergy, or some extensions 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-mechanical and (in Part II) separation operations and are found in heat and mass exchangers, thermal networks, energy convertors, 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 dynamical 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. In this (first) part of work we restrict to dynamic limits on work that may be produced or consumed by a single resource flowing in an open heat-mechanical system. To evaluate these limits we consider sequential work-assisted unit operations, in particular those of heating or evaporation which run jointly with "endoreversible" thermal machines (e.g., heat pumps). We also compare structures of optimization criteria describing these limits. In particular, we display role of endoreversible limits in conventional operations of heat transfer and in work-assisted operations. Mathematical analogies between entropy production expressions in these two sorts of operations are helpful to formulate optimization criteria in both cases. Finite-rate 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; Finite-time thermodynamics; Heat pumps; Endoreversible engines; Exergy; Thermodynamic limits; Second law

1. Introduction: Energy limits by thermodynamic optimization

Voluminous literature on separation and exchange operations may be found, especially in the field of optimization of separation units and heat and mass exchangers. This literature often deals with very diverse, single-stage and multistage separation units and variety of many complex systems composed of such units; optimizations run usually with either technical or economic criteria with visible tendency towards complex process economies. There are also efficient mathematical techniques to solve related ordinary or partial differential equations. However, mathematics seems to be mainly a standard tool in this context. What is really novel therein is a unifying, integrated concept of the dynamical (finite time) limits for energy production or consumption. The integrating nature of these limits is important. Traditional chemical engineering approaches

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0017-9310/02/$ - see front matter
PII: S0017-9310(02)00017-0

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 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 nth stage
q_1	driving heat in the engine mode of the stage
$R^n(\boldsymbol{x}, t)$	optimal work function of cost type in terms of state and time
S	solid 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 kth component,
μ'	coefficient of outlet gas utilization
τ	non-dimensional time, number of the heat transfer units (x/H_{TU})

Subscripts

g	gas
i	ith 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 kth or nth stage

Abbreviations

EGM	entropy generation minimization
FTT	finite-time thermodynamics

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. As the consequence of such approaches an engineer is perplexed whenever he has to shift his design from one to another operation, and the most of his past experience is of little use.

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. The dynamic limits are not only stronger than static, the consequence of finite rates, but also are more useful in design. Our interest is in revealing and systematizing such generic limits, and this is an original feature of our approach, not encountered in previous works on energy problems. These limits may, for example, determine lower bound for the amount of the energy supply, exploitation costs, amount of a key substance, investment, equipment dimension, etc. They describe limitations that an engineer will encounter during his design of exchange or separation units running with a prescribed minimal intensity (local or average). Some bounds are so natural and simple (as, e.g., that on the lowest heat consumption), that one may confuse them with the well-known thermostatic limitations. Still, the bounds we are looking for are not classical bounds encountered in textbooks on thermodynamics and separation science. Those classical 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 considerably higher than those classical ones known from the textbooks. Consider, for example, the heat consumption in a distillation column and evaluate a realistic bound that corresponds with the lower limit of heat associated with the use of the theoretical plates instead of the real plates of certain unknown efficiency (lower than unity), in the same column. This bound is usually 2–3 times larger than another (lower) bound, the heat consumed at minimum reflux conditions (already a quite artificial quantity as it pertains to a column with infinite number of theoretical stages). Next, the heat at minimum reflux is usually several times larger than the reversible evaporation heat. In effect, a design engineer must expect that, in the considered case, the heat consumption he should assume should be at least of the order of magnitude higher than the evaporation heat. In complex separation processes as those involving cycles, losses, and non-linearities such evaluations are highly nontrivial. 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 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]. Such applications would never be possible without extracting an abstract conceptual tissue from the material that was previously generated for separators and thermal engines.

Recent works on second law analyses 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 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 cumulative exergy consumption and exergy of the considered product. In ecology, ecological counterparts of these quantities are introduced. Consequently, in ecology, the so-called ecological cost is introduced as the cumulative consumption of exergy of unrestorable resources burdening a definite product. Technical indicators obtained from related analyses are used to forecast changes in demand for heat agents caused by changes in production level and technology of product yield and changes of costs of heat agents. This is a way to obtain information about diverse energy-consuming (more exactly: exergy-consuming) technologies, and this is also a way to compare these technologies. Finally, 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 sole notion of the classical exergy seems insufficient without including the associated notion of minimal (residual) dissipation of this exergy. This is, 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. Limits following from reversible processes are most often too far from reality to be most useful.

However the method of cumulative exergy costs 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 burden by sorts, locations and dates of various technologies, the property that usually change process efficiencies, semiproducts, controls, etc., and thus influence the cost definition. One way to improve the definition in question 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 costs, was 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 remained largely unknown. In fact, the cumulative costs are not functions but rather functionals of controls and state coordinates, otherwise optimal costs have properties of functions (potentials). To ensure potential properties for optimal costs to deal with the analyses efficiently, their definition should propose a method that would eliminate the effect of controls. Yet, the original definition of the cumulative exergy cost [2] does not incorporate any approach that would eliminate the extend effects of (controls etc.) the property that makes this definition inexact and inobjective.

The solution to the above difficulties was recently found in the series of work in FTT [3]. Therein the potential cost functions are generated via an optimization, i.e., potentials are found which involve extremal (minimal or maximal) values of the underlying cost criteria with respect to controls but not states. The mathematical structures of these cost criteria as discrete and continuous functionals (not functions) were first recognized in FTT.

2. Diverse engineering operations and extended potentials

In both FTT and optimal control approaches, the optimization of the cost expression (or an associated entropy production) automatically eliminates controlling parameters from the cost criteria, thus generating a potential (R or R_σ). For a definite operation, the potential depends only on initial and final states, duration and (in multistage processes) total number of stages. 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 [1,4]. 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].

Engineering processes are most often far from equilibrium processes (i.e., outside of the realm of linear irreversible thermodynamics), they must go to the desired extent of completion within a finite time, and they must produce at least a minimum amount of product. Furthermore, efficiency based solely on physical grounds is more often than not an insufficient criterion for the performance of a chemical engineering process. Economic and ecological considerations also play important roles. All this means that classical equilibrium thermodynamics can at most place lowest limits on chemical engineering processes and that one must turn to irreversible thermodynamics for more information.

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 basis, [7]. Therefore, one can ask whether any real process operates close enough to the reversible limit for the traditional measures to be useful or even relevant. If not, is it possible to extend the concepts of reversible thermodynamics to provide limits for the performance of processes constrained to operate in finite time or at non-vanishing rates? If yes, what are the optimal paths related to the finite-time transitions? These questions arose from the need to evaluate how effectively real devices and real industrial processes use energy, from the viewpoint of their own limits rather than the reversible process limits. They stimulated efforts to find bounds described by certain potentials corresponding to a given process performed in a finite time [8,9], in particular the thermodynamic bounds defined by the minimal values of the total exergy dissipated or the total exergy driving a finite-time process [10]. The choice of optimization criteria can, of course, affect the optimal performance and the corresponding bounds.

FTT investigates the effects of constraints on time and rate on the optimal performance of generic processes through integral or sum expressions describing $\sum \Delta S_k^{\mathrm{i}}$, $\sum \Delta B_k^{in}$, $\sum \Delta B_k$, W, or their generalizations including cost-type criteria, rather than pursuing the irreversible equations exclusively. Usually the goal of an FTT analysis is: (1) to find the paths of minimum $\sum \Delta B_k^{in}$ or $\sum \Delta S_k^{\mathrm{i}}$ 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. Note that these bounds are in general functions of state and duration rather than numbers. They generalize the well-known thermostatic bounds for finite time and/or rates. They are limits from the standpoint of the "thermodynamic costs of the driving exergy", $K^{in} = \sum \Delta B_k^{in}$, or a similar criterion, and they should not be identified with actual values of $\sum \Delta S_k^{\mathrm{i}}$ or $\sum \Delta B_k^{in}$ in an actual process which should run under an economic rather than a thermodynamic optimum. 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 non-linear 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, e.g. thermal resistances between the reservoirs and working fluid (Curzon and Ahlborn cycle [16]). Many results, even those generated by purely classical analyses, are new. For example, recent results [17] show that when a part of the dissipated energy remains within the system, not all of the availability is necessarily lost. The bound defined by the thermodynamic length no longer limits the availability losses but rather a so-called work deficiency, W_{d} (where usually $W_{\mathrm{d}} > -\Delta A$), or the total loss of availability that would have resulted if all the available work were lost to the environment [17].

The solution of a thermoeconomic 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]. Nevertheless, a number of complex economic and ecological analyses have been born as generalizations of thermodynamic irreversibility analyses. While various performance criteria hold for various problems (this variety has already been admitted by extended versions of FTT), the physical constraints are the product of thermodynamic analyses. Even if one replaces thermodynamic criteria by economic ones, the same optimum search method can often be used in both cases. Most of the methodological experience gained from the formulation of mathematical models of optimization can be preserved when passing from thermodynamic to economic optimization.

From the standpoint of thermoeconomics, optimization of the driving or propelling 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 summarized by various researchers [20–23]. On the other hand, approaches to "optimal design" type that use the entropy (or exergy) generated as their optimization criteria make little sense from the standpoint of economic design. While the finite time bounds obtained via such optimizations can be of value in placing certain realistic limits on the use of the exergy and resources, the design itself can in this case correspond at best to the minimum of the exploitation costs (approximated by the exergy costs K). Sometimes this minimum may even require infinitely large equipment as in the case of rectification. The difference in the role played by ΔS^{i} and $K = \Delta B^{\mathrm{i}}$ in obtaining the limits on the use of resources and in design has been largely overlooked in many works.

Curzon and Ahlborn [1,16] showed that a heat engine with heat resistances between the reservoirs and the working fluid can operate between two extreme zero-power limits (power being defined as work per cycle time). One extreme is the reversible, Carnot limit at maximum (Carnot) efficiency. This is the limit where the engine cycles extremely slowly (quasistatically); the efficiency is high, but the engine performs too few cycles to deliver much power. If the engine cycles too fast it operates inefficiently because it does not get hot enough or cold enough to ensure that the ratio of the two extremal temperatures of the working fluid, T_1'/T_2', is much less than 1. Hence the other extreme is the "thermal short circuit" limit of zero power at zero efficiency. Heat engines are usually designed to operate somewhere between the limit of the reversible maximum of efficiency and that of maximum power [24]. The Curzon–Ahlborn efficiency at maximum power is $\eta_{\mathrm{mp}} = 1 - (T_2/T_1)^{1/2}$, regardless of the heat transfer coefficients and other material properties. The original concept of Curzon and Ahlborn has been extended to a richer spectrum of problems in FTT by taking the main sources of dissipation (e.g., finite heat conductances) into consideration. This leads to even more realistic bounds on performance. Curzon and Ahlborn analyzed 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 [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. (See the lucid power-efficiency diagrams by Gordon [26]). The power-efficiency curves exhibit a maximum power point and a maximum efficiency point, the latter usually being well below the Carnot efficiency. Time-dependent driving functions that maximize power when heat input and heat rejection are non-isothermal and the effects of friction on the optimal solution have been determined [27]. The optimal performance of an engine which operates between a finite high temperature source and an infinite heat reservoir and obeys the heat transfer law of Onsager thermodynamics ($q = K'\Delta T^{-1}$) has been compared with the performance predicted for Newton's law of heat transfer [28]. The analysis 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. Three heat-source cycles using low-level heat sources such as solar energy, geothermal energy and waste heat have been analyzed in a unifying treatment [29].

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. It includes the effect of entropy production σ and simplifies to the classical result in the limit of vanishing σ. These results show some resemblance to those known for the efficiency of thermal engines evaluated at the maximum power point.

For any finite rate separation process with a given non-vanishing mass flow (average mass flow in the case of cyclic processes) the exergy consumption is larger than the corresponding reversible consumption. Since the constraint on the feed flow (and any other constraints on e.g., boundary concentrations) is operative, only a part of the entropy produced can be reduced through an optimal choice of an operational parameter. For a given feed flow such a reduction causes a related decrease in the valuable heat; hence, the minimum of the heat consumed corresponds indeed to the minimum of σ. Thus, there exists a more realistic lower bound, greater than the classical value, on the valuable heat consumed. This bound is a function of the flow F. Any real separation process with a given feed flow will consume an amount of heat that cannot be lower than this limit. This value is still just a lower bound and is not the economically optimal heat consumption for any particular separation unit. Whatever the economical heat consumption is, for a given operational situation this consumption cannot be less than this lower bound. Knowledge of this bound is of value for design.

A chemical engineer realizes however that it is not necessary to speak about entropy production at all in order to determine the lower bound on heat consumption. One could simply minimize the heat as a function of a parameter at given operational constraints. However, entropy production (or exergy dissipation) is a convenient common measure of the imperfection of very diverse processes. Yet the rate constrained thermodynamic bounds of FTT may implicitly contain a constant vector of certain non-thermodynamic quantities (e.g., design parameters). Care is necessary when their application to design, where this vector may change, is in question. The difference between FTT 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 minimum of entropy production. In conclusion, real columns should never be designed to operate at the bound of minimum heat (or minimum σ) even if this is not a thermostatic limit. However, for existing plants where the investment is fixed or its variation can be ignored cumulative costs and second law analyses are more useful.

Non-traditional energy sources have recently begun to become economically realistic. Examples are 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, and references therein]. Upper and lower limits for the coefficient of performance of solar absorption cooling cycles have been derived from the first and second laws [37]. These limits depend not only on the environmental temperatures of the cycle components but also on the thermodynamic properties of refrigerants, absorbents and mixtures thereof. Quantitative comparative studies of different refrigerant–absorbent combinations are now possible.

All chemical processes consume unrestorable natural resources; the quicker civilization develops, the sooner these are exhausted. Exergy was 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 [38,39,41–44]. The exergetic ecological costs are of little use in true optimization of production processes, even from the viewpoint of minimization of the consumption of natural resources. The indices of ecological costs determining the extent to which technological processes exhaust natural resources have been summarized [45]; apparent analyses of chemical processes are also available [46]. One example treats the ecological second law analysis of heat delivery from a complex heat-power station; the minimization of the consumption of unrestorable natural materials uses the exergy [41]. Cumulative exergy cost seems to be suitable for industrial chemistry. However, it is not any proper measure of energy limits since these are purely physical quantities. In fact, as stated in Section 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 optimal costs, their definition must eliminate effect of controls and external parameters. This is ensured in the method that deals with *optimized* physical costs as energy limits. That method is discussed below. In fact, as we shall see soon, cumulative costs are not functions but rather functionals of controls and state coordinates, and that only optimal costs acquire properties of functions (potentials).

3. Energy limits for sequential operations with heat exchange

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. We also compare the developed optimization criteria for work-assisted operations with those for conventional operations (without work). As our method rests on thermodynamics, it can deal with arbitrary participating fluids, including, in particular the radiation fluid. For that fluid the endoreversible limits incorporate, as a sole effect, a minimum entropy production caused by simultaneous emission and absorption of radiation. This means that limits for solar-assisted drying operations can also be treated by the method presented here. The method involves generally an optimization of power and/or related work from an endoreversible sequence of thermal machines thus generalizing the well-known method of evaluation of the classical exergy in reversible sequences [46,47]. The problem of finite-rate limits, which was briefly outlined in an earlier paper [48], requires sequential operations with thermal machines [49–51], such as multistage heat pumps, where total power input is minimized at constraints which 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 [52]. The principle of one-stage operation on T–S chart is explained in Fig. 1, whereas the topological scheme of the multistage power consumption leading to generalized exergies of heat-pump modes is illustrated in Fig. 2.

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 general philosophy of optimization [53]. Formal analogies do exist between entropy production expressions in work-assisted and in conventional operations which are helpful to develop suitable criteria and models. In this paper we evaluate endoreversible limits through optimization of sequential work-assisted and solar-assisted operations which extend well-known classical operations without work such as conventional heating, evaporation and drying. Constraints take into account dynamics of heat and mass transport and rate of real work consumption. Finite-rate, endoreversible models include irreducible losses of classical exergy caused by resistances. Extremum performance functions for optimal work, which incorporate residual minimum entropy production, are determined in terms of end states, duration and (in discrete processes) number of stages. Analogies between entropy production expressions for work-assisted operations and those without work help formulate optimization models of the former.

To start with a quantitative example we consider the heat transfer-driven work generation (consumption) in

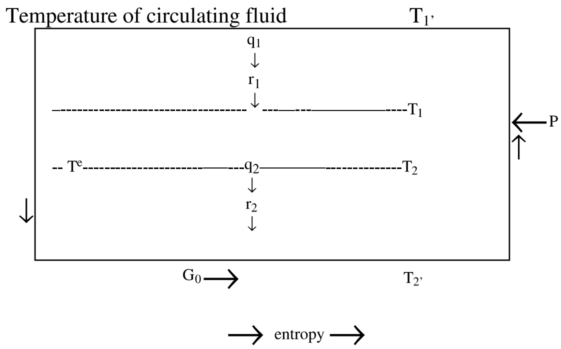

Fig. 1. Scheme of designations and temperature relations on the T–S chart for an irreversible one-stage heat pump ($\eta_C \leqslant \eta \leqslant 1$).

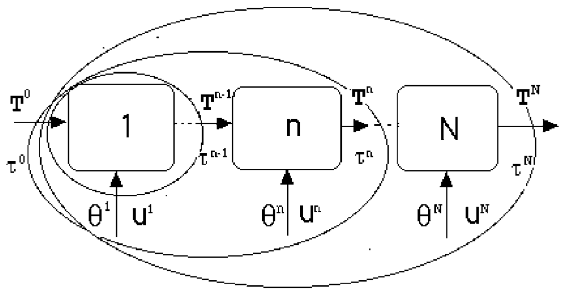

Fig. 2. Multistage process of energy utilization for fluid at flow optimized by the forward algorithm of dynamic programming. The stage-size control is θ^n and the remaining controls are components of vector $\mathbf{u}^n$. In Bellman’s Optimality Principle ellipse-shaped balance areas embrace successive subprocesses which evolve by inclusion of remaining stages.

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 multistage production (consumption) of work requires the use of the sequence of stages, Fig. 2. 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. The fluids are of finite thermal conductivity, hence there are finite thermal resistances in the system. In a multistage heating operation the fluid's temperature increases at each stage; the whole operation is described by the sequence $T^0, T^1, \dots, T^N$. The popular 'engine convention' is used: work generated in an engine, W, is positive, and work generated in a heat pump is negative; this means that a positive work $(-W)$ is consumed in the heat pump. The sign of the optimal work function $V^N = \max W^N$ defines the working mode for an optimal sequential process as a whole. In engine modes $W > 0$ and $V > 0$. In heat-pump modes, $W < 0$ and $V < 0$, therefore working with a function $R^N = -V^N = \min(-W^N)$ is more convenient. 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 functions V^N are generalization of the classical exergy in discrete processes with finite durations.

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. For any finite reservoir, the state space of the overall (bath-containing) system would necessarily involve variable bath coordinates, and the system dynamics would then be influenced by a difference dynamics describing the bath history in terms of these variable coordinates. However, 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 involved as the reservoir-history independent. In fact, due to the infiniteness of the reservoir, the system's history is expressed exclusively in terms of the resource fluid coordinates and their time derivatives. Moreover, the potential function of extremum work, which is obtained via optimization of a work integral, is of exergy type. This means that the function contains the intensive coordinates of the bath as parameters accompanying the state coordinates of the finite-resource fluid.

Our use of extremum seeking methods in sequential systems with work producers or consumers could, perhaps, make an impression that the goal here is an economic optimization of real thermal machines and/or their diverse topological arrangements, which, in general, are called thermal networks. Should such optimization be the case, a thermal system could be optimized via a customary approach which would require: a detailed network modelling, inclusion of economic accounting, and occasional imbedding of the optimized system into a broader environment to include interacting chains. In fact, the range of optimizing 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 exergy-like 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. In a definite real system, a weak link may be observed when making the exergy balance for participating streams, which is the usual procedure made in the so-called second law analyses or thermoeconomic optimization. As a maximum of what can be got from comparison, one could then achieve a balance which involves exergy changes of streams and which resembles the economic balances appearing in customary optimizations. By considering Figs. 3 and 4 one may compare scheme of a drying process with endoreversible heat pump with a scheme of a real drying process with a heat pump.

In the endoreversible case the perfect (second-law) efficiency of the Carnot (work-producing) engine across 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. In fact, the restriction to external irreversibilities is unnecessary, and FTT models can go beyond "endoreversible limits" to treat internal irreversibilities as well, see Eq. (59) below and [55]. It is most essential, however, that in either of 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

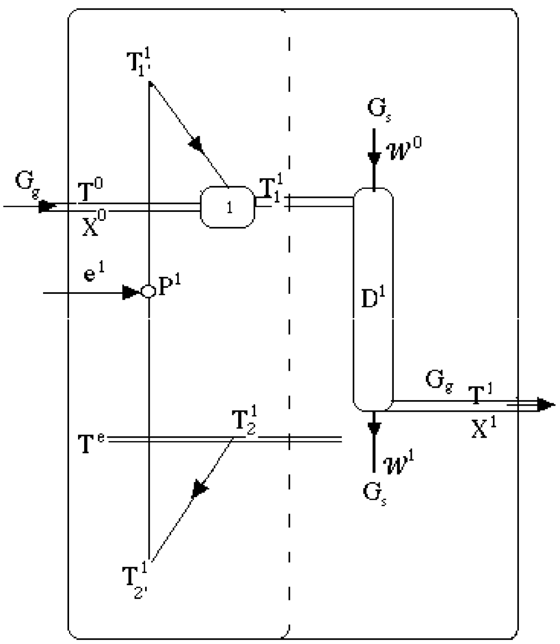

Fig. 3. A scheme of one-stage drying process with an endoreversible heat pump.

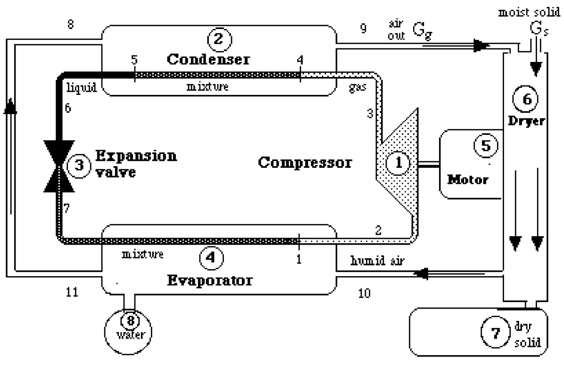

Fig. 4. A scheme of a real drying process with a heat pump.

on energy consumption or production are stronger then those predicted by the classical exergy. In short, this results from the "process rate penalty" that is taken into account in every version of FTT.

In the hierarchy of limits resulting from more and more detailed models, the limits of the second and higher versions of FTT are, of course, stronger than the limits of the first (endoreversible) version. The weakest or the worst are limits of classical thermodynamics, resulting from the classical exergy; for the latter function see [46]. When restricting to endoreversible limits no real thermal machines are needed; what we need are perfect energy convertors (the Carnot jumps) and perfect external dissipators. In the classical Carnot analysis the resource and environment reservoirs are insensitive to the effect of dissipators (boundary layers, resistances, etc.) because the reversible static situation requires thermal homogeneity of each reservoir in the space. In the irreversible analysis, performed here, which admits dissipative transports in reservoirs, the inhomogeneities of transport potentials play a non-trivial role. In contrast, for the purpose of a real-system optimization, an endoreversible model of two interacting reservoirs would be rather insufficient, or even irrelevant. When calculating energy limits, we search for (hierarchy of) diverse, *purely physical* extrema with no regard to economic optima. In real systems the energy conversion does not occur in Carnot units, there are many streams, not one, and internal irreversibilities are as a rule essential. Yet, for the purpose of enhanced bounds, the endoreversible sequence of single-stream states is the next step in comparison with the purely reversible sequence leading to classical exergy [46]. Further steps (higher rank limits) are possible [3,55].

4. Controls restricted by entropy balance and operations with pure heat flow

We begin with a single-stage engine in the standard Novikov–Curzon–Ahlborn operation (NCA engine) in which c is resource's specific heat, and g_1 and g_2 are thermal conductances [3], the products of heat transfer areas and heat transfer coefficients. We shall treat a relatively unknown formulation in which the power of the engine is maximized with respect to both the temperatures of circulating fluid, T_1' and T_2', that are constrained controls. The constraint is the entropy balance of the reversible part of engine. The constraining equation is handled by the method of the Lagrange multipliers. In this formulation the power yield is expressed by an equation

$$P = g_1(T_1 - T_1') - g_2(T_2' - T_2). \tag{1}$$

For the engine mode of the system, this equation describes the difference between the driving heat flux and the flux of rejected heat, $P = q_1 - q_2$. The entropy balance constraint

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

is used here in the form of the continuity of entropy flux. Thus the two decisions, T_1' or T_2', in Eq. (1) are linked by Eq. (2). The modified optimization criterion that adjoins the constraint (2) to power function (1) by the Lagrange multiplier λ has the form

$$\begin{aligned} P' &= P + \lambda C \\ &= g_1(T_1 - T_1') - g_2(T_2' - T_2) \\ &\quad + \lambda\left(\frac{g_1(T_1 - T_1')}{T_1'} - \frac{g_2(T_2' - T_2)}{T_2'}\right). \end{aligned} \tag{3}$$

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'

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

Explicitly, the following set of equations should be solved

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

$$(P')_{T_2'} = -g_2 + \lambda(-g_2)\frac{T_2}{(T_2')^2} = -g_2\left(1 + \lambda\frac{T_2}{(T_2')^2}\right) = 0, \tag{6}$$

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

Of course, the last equation is the recovered entropy constraint as the extremum condition of P' with respect to λ. The solution of Eqs. (5) and (6) with respect to λ is

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

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

Hence the temperatures of the circulating fluid are linked by an equation

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

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 this expression for T_1' into the equation of the entropy balance we obtain

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

Whence after rearrangements, the temperature T_2' follows as

$$T_2' = \frac{g_1\sqrt{T_1T_2} + g_2T_2}{g_1 + g_2}. \tag{13}$$

Next, with Eq. (11), temperature T_1' is obtained

$$T_1' = \frac{g_1\sqrt{T_1T_2} + g_2T_2}{g_1 + g_2}\sqrt{\frac{T_1}{T_2}} = \frac{g_1T_1 + g_2\sqrt{T_1T_2}}{g_1 + g_2}. \tag{14}$$

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. (13) and (14)

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

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 and less lucid. However, for a modified but still equivalent form of criterion (1),

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

extremum Lagrange multipliers are different from those described by Eqs. (8) and (9) although the resulting conditions (10) and (11) are still the same. This difference is the consequence of different objective functions applied in each case while preserving the same constraint. That example proves that endeavors to attribute physical significance to Lagrange multipliers should be made carefully. The physical significance of λ is not objective with respect to transformation of constraints. Examples of this sort are also known in the variational hydrodynamics of perfect fluid [13]. Clearly, however, the approach using Lagrange multipliers leads to solution in a shortest time and applies the way that is methodically the simplest. All controls are treated on an equal footing, and the original expression for the optimization criterion does not need to be transformed. The optimal solution includes all controls in terms of states of two fluids participating in the operation, (T_1, T_2). Moreover, the optimal decisions satisfy identically process constraints, in our case the entropy balance of the energy generator. Equation (11) remains valid if a constant entropy source is assumed in Eq. (2). Yet in this case Eqs. (17) and (18) become more complicated and predict worse powers and efficiencies.

5. Carnot temperatures as optimized controls in problems of extremum power

Recently, the so-called Carnot temperatures (also called driving temperatures) were proposed to effectively describe various work-assisted operations [50]. In terms of these quantities, the structural properties of the active heat exchange in systems in which two boundary layers are separated by the Carnot engine, the actual efficiency is always given by the Carnot formula. To illustrate that idea we continue considerations on a single-stage NCA engine [3]. In systems with power production the condition of the energy flux continuity does not hold. It is just the power produced P which constitutes the difference between the two heat fluxes. Thus the continuity of q cannot be a condition to derive the traditional notion of the overall heat conductance, $g = (1/g_1 + g_2)^{-1}$. It is well known, however, that the traditionally defined overall heat conductance, g, does appear in equations of linear thermal systems with power production [1,3]. In fact, the traditional overall conductance g emerges naturally in models of linear power production systems provided that specific control variables 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.

Efficiency of 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 satisfied by the Carnot formula

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

where 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' from this equation yields

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

In the entropy balance expressed in terms of temperatures of the circulating medium, T_1' and T_2',

$$\frac{g_1(T_1 - T_1')}{T_1'} - \frac{g_2(T_2' - T_2)}{T_2'} = 0, \tag{2'}$$

we eliminate with the help of Eq. (21) one of the temperatures of circulating fluid T_1' or T_2'. Doing this, for example, with temperature T_2' we substitute Eq. (21) into (2′) to obtain

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

or

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

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

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

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

In processes with pure 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, in order 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 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 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, as we shall see later, the forms of the kinetic equations (25) and (31) are constrained to fluids with Newtonian heat exchange.

Summing up we conclude the following. By comparing the 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 have shown that the first Carnot temperature satisfies the expression $T' \equiv T_2 T_1'/T_2'$. This ensures the classical Carnot formula for the efficiency of irreversible engine in the form $\eta = 1 - T_2/T'$. Similarly we have shown that the second Carnot temperature satisfies $T'' \equiv T_2 T_1'/T_2'$; this ensures the Carnot formula in the form $\eta = 1 - T''/T_1$. The comparison of both expressions for η yields the relation $T_1 T_2 = T' T''$, which is the constraint condition that was sought. General properties of Carnot controls are illustrated in Figs. 5 and 6.

Let us now discuss problems of power optimization with the use of Carnot temperatures as decision variables. As previously, the constraint is represented by the entropy balance (2′) which, however, must be written down in terms of Carnot variables, T' and T''. The heat fluxes and power P are expressed in terms of the first and the second Carnot temperatures

$$q_1 = g(T_1 - T'), \tag{25'}$$

$$q_2 = g(T'' - T_2), \tag{31'}$$

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

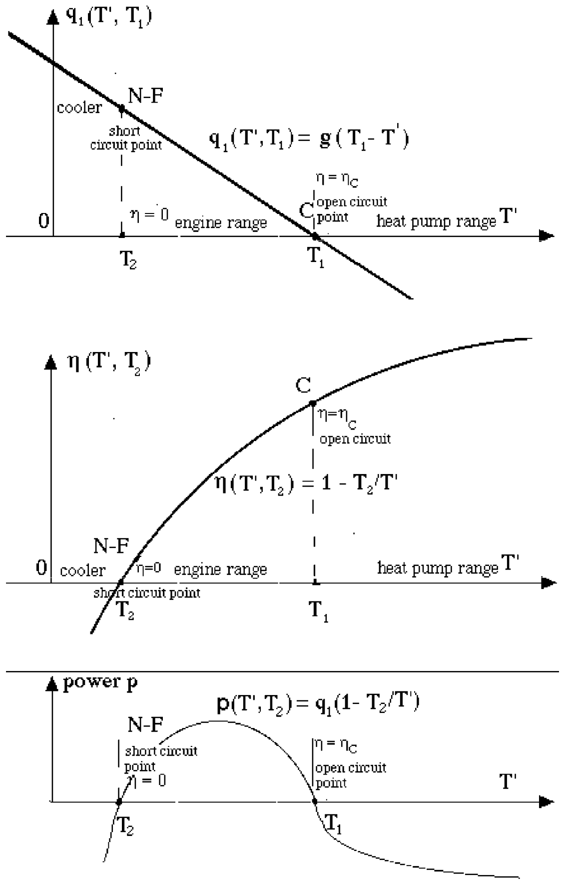

Fig. 5. In terms of the Carnot control T' classical thermodynamic relations and formulas for processes without work are extended to irreversible processes with work production or consumption.

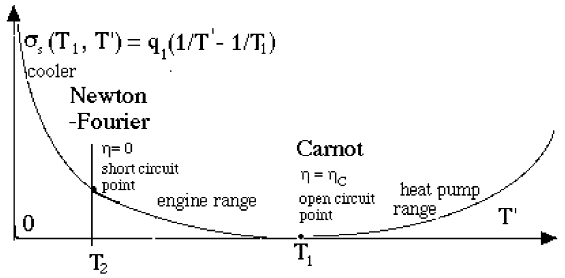

Fig. 6. In terms of the Carnot control T' classical thermodynamic expressions and diagrams for the entropy production in processes without work are extended to processes with work production or consumption.

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 form of the traditional (Newtonian) heat exchange. The substantiation for the Newtonian structure of expressions describing heats q_1 and q_2, which contain the overall conductance g, was first found in the earlier work [50]. As shown below, the connection between the first and second Carnot temperature may be interpreted as a special form of the equation of continuity for the entropy flux. In the method of Lagrange multipliers, this connection is treated as an implicit constraint (the one, which does not serve elimination of any control). In the subsequent text we shall exploit only those properties T' and T'', which are essential in analysis of the maximum power, P.

We shall now show 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 related Carnot temperatures in expressions describing heat fluxes in the entropy balance based on temperatures of the circulating medium, T_1' and T_2'

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

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 for the engine efficiency in terms of these temperatures and the first Carnot temperature, T', Eq. (20), and then calculate T_2' in the form $T_2' = T_2T_1'/T$. 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

$$\begin{aligned} P' &= P + \lambda C \\ &= g\big(T_1 + T_2 - T' - T''\big) + \lambda\big(T_1T_2 - T'T''\big). \end{aligned} \tag{36}$$

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

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

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

The necessary condition for extremum

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

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

$$g + \lambda T'' = 0, \tag{40}$$

$$g + \lambda T' = 0, \tag{41}$$

$$T_1T_2 = T'T''. \tag{42}$$

From the first and the second equations, 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 this result into the constraint (33) one can evaluate optimal values of T' and T'':

$$(T')^2 = T_1T_2, \tag{44}$$

$$T' = \sqrt{T_1T_2}, \tag{45}$$

$$T'' = T' = \sqrt{T_1T_2}. \tag{46}$$

The optimal efficiency is then $\eta = (1 - T_2)/T' = (1 - T_2)/\sqrt{T_1T_2}$, i.e., Eq. (18) is valid. The maximum power equals

$$\begin{aligned} P &= g(T_1 + T_2 - \sqrt{T_1T_2} - \sqrt{T_1T_2}) \\ &= g(T_1 + T_2 - 2\sqrt{T_1T_2}) = g(\sqrt{T_1} - \sqrt{T_2})^2. \end{aligned} \tag{47}$$

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 in work-assisted exchangers. The traditional exchangers (without work) are described by properties: $\eta = 0$, $T' = T_2$, $T'' = T_1$. These do not refer, however, to the point maximizing power P, but to the so-called "short-circuit" point. For the latter both temperatures of circulating fluid are equal, $T_1' = T_2'$, $P = 0$ and the same heat flux flows through the two resistances, $q_1 = q_2$. In terms of Carnot variables the theory of traditional exchangers is a particular case of the theory of work-assisted operations. Also unifying for both sort of operations are analytical expressions and diagrams describing losses of maximum work and entropy production, Figs. 5 and 6.

6. Modelling and optimization of power fluxes in multistage systems

We shall continue the presentation of the use of Carnot variables. In this section we focus on 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 utilization [3]. Next we pass immediately to multistage sequential operations. In the one-stage operation temperature of the driving fluid changes between T^0 and T. The utilized heat flux which leaves the condenser equals $q_1 = -G_f c(T - T^0)$, where G_f is the fluid flow and c-fluid's specific heat. Fig. 3 depicts the application of the operation to (say) drying with an endoreversible heat pump, whereas Fig. 4 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, and 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. Casting the problem in the format of the discrete maximum principle we arrive at the discrete functional of consumed work

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

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 non-dimensional 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

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

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 apart 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 evaluation of the classical exergy [46], but is strongly dissimilar to calculation of the cumulative exergy cost [2,39,41] that is influenced by economic terms and, therefore, is neither an objective economic quantity nor a physical energy limit. Eq. (49) describes the work supplied to the process in which the controlled 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 equality $u = \mathrm{d}T/\mathrm{d}t$ which is valid for the temperature representation of the heat q_1 per unit overall conductance,

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

Eq. (51) refers to a continuous process in which the fluid (heated in an infinite sequence of inifinitesimal heat pumps or cooled in an infinite sequence of inifinitesimal engines) changes its states between the initial temperature T^i and the final temperature T^f. The first term is the reversible thermodynamic 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 non-dimensional 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 by an equation

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

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

Eq. (51) proves that it is the entropy production that causes the non-potential component of the work integral. We note that minimizing the entropy production in a fixed-end sequential problem assures minimum of the work consumption in the heat-pump mode and maximum of work production in the engine mode. Since the first or potential term is path independent, the (non-potential) entropy production determines the property of the extremal trajectory. Therefore a common differential equation holds for extremals of extremum work and minimum entropy production [51]. For the continuous modes we find an equation

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

Eq. (53) is satisfied by function $T(t)$ which solves the simple differential equation, $\dot{T} = \xi T$, where the constant ξ is the rate indicator which is positive for fluid's heating and negative for fluid's cooling. With the boundary conditions for $T_1 (T_1 = T^{\mathrm{i}}$ at τ^{i} and $T_1 = T^{\mathrm{f}}$ at $\tau^{\mathrm{f}})$ we conclude that an unconstrained extremal path is an exponential curve $T_1(\tau) = T_1^{\mathrm{i}}(T_1^{\mathrm{f}}/T_1^{\mathrm{i}})^{\tau/\tau^{\mathrm{f}}}$ consistent with the following Carnot-temperature control

$$T'(\tau) = T_1(\tau)(1+\xi) = T_1^{\mathrm{i}}(T_1^{\mathrm{f}}/T_1^{\mathrm{i}})^{(\tau-\tau^{\mathrm{i}})/(\tau^{\mathrm{f}}-\tau^{\mathrm{i}})}\left(1+\frac{\ln(T_1^{\mathrm{f}}/T_1^{\mathrm{i}})}{\tau^{\mathrm{f}}-\tau^{\mathrm{i}}}\right), \tag{54}$$

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

Consider now extremals of the underlying multistage process, Eqs. (49) and (50). Since the discrete model is linear with respect to the time interval θ^n, a discrete algorithm with a constant Hamiltonian governs the optimal multistage process [52,53]. The optimal discrete dynamics has the form

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

which is the discrete analog of Eq. (55). The optimal solution asserts that $\theta^n = \theta^{n-1}$ and $(T^n)^2 = T^{n-1}T^{n+1}$. This property ensures that the temperatures T^n between the stages n and $n+1$ are geometric means of the boundary temperatures. The Carnot temperatures, T'^n, which assure that optimal trajectory are

$$T'^n = T^n(1+\xi) = (T^N)^{n/N}(T^0)^{[n(N-1)/N]-(n-1)} \times \left(1+\frac{N}{\tau^N-\tau^0}\left[1-\frac{T^0}{T^N}\right]^{1/N}\right). \tag{56}$$

The discrete solution converges to the exponential solution of Eq. (53) in the limit of an infinite N. In fact, Eq. (56) is a discrete generalization of the optimality condition known for optimal controls of heat exchangers and simulated annealing [54–58]. For exergy boundary conditions, the optimal work associated with Eq. (56) is a discrete generalization of the continuous finite-time exergy [51]. Yet we should keep in mind that here we have found an irreversible (finite time) limit of work through the "endoreversible imbedding" of the Carnot operation within the dissipative system, and after recognition that system is capable of upgrading and utilizing finite resources. See Eq. (59) for non-Carnot generators.

The structure of the control equations shows that the driving temperature T' can be interpreted as the quantity replacing the upper temperature T_1' of the thermal machine in the general case when both conductances g_1 and g_2 are essential. Whenever the effect of the second resistance (g_2^{-1}) is negligible, $T' = T_1'$. Indeed, when g_2^{-1} tends to zero, $T_2' = T_2 T^{\mathrm{e}}$, thus, from Eq. (14′), $T' = T_1'$, and the control equations are valid for the temperature T_1'. However, the crucial statement which explains how to obtain T' follows from the equality $T' = T_2$ at the state in which work is not produced (the so-called "short-circuit point" of the system, where $\eta = 0$). This leads to the theorem: *the analytical expression for the Carnot temperature T' can be obtained from the analysis of the short-circuit point by solving the energy (mass) exchange equations in which T' replaces T_2 or T^{e}. The solution to these equations should be found for the temperatures T_1' and T_2' in terms of the common heat flux q_1; after making the identification $T_1' = T_2'$ the temperature T' follows in the form $T' = f(T_1, q_1, g_1, g_2)$.*

7. Common treatment 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

$$\begin{aligned} R(T^{\mathrm{i}}, T^{\mathrm{f}}, \tau^{\mathrm{f}}-\tau^{\mathrm{i}}) &\equiv \min(-P/G_{\mathrm{f}}) \\ &= \min\int_{\tau^{\mathrm{i}}}^{\tau^{\mathrm{f}}} c(T)\left(1-\frac{T^{\mathrm{e}}}{T'}\right)(T'-T)\,\mathrm{d}\tau \\ &= h(T^{\mathrm{f}}) - h(T^{\mathrm{i}}) - T^{\mathrm{e}}\left(s(T^{\mathrm{f}}) - s(T^{\mathrm{i}})\right) \\ &\quad + T^{\mathrm{e}}\min\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} c(T)\frac{(T'-T)^2}{T'T}\,\mathrm{d}\tau. \end{aligned} \tag{57}$$

This equation refers to the endoreversible limit, but it may easily be generalized to processes with internal dissipation as we shall show soon. Likewise, the maximum work in the engine mode is described by the optimal function $V = -R$. In both cases T and T' are linked by the differential constraint

$$\mathrm{d}T/\mathrm{d}\tau = T' - T. \tag{58}$$

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 limits which involves an internal dissipation in the participating thermal machine? We need to recall the hierarchy of limits stressed in Section 1. For limits of higher rank, an internal entropy generation characterized by a parameter

p is included in the dissipation model and then Eq. 57 is replaced by its simple generalization

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

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 a 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. What is important then is a proper compromise associated with the accepted limit of a finite rank. For limits of various ranks, inequalities are related to R and real work W^{real} that are valid in the form $W^{\mathrm{real}} > R^k \cdots > R^1 > R^0$, where R^1 refers to the change of "endoreversible exergy", and R^0 pertains 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 the consideration of any 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 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 the non-dimensional time τ defined as $\tau = G_{\mathrm{g}}c_{\mathrm{g}}/(G_{\mathrm{s}}c_{\mathrm{s}})$, Eq. (58) describes the temperature change of the dispersed phase in a process in which the gas crosses vertically the bed of the granular solid in a horizontal heat exchanger (HFE). A suitable assumption here is that the equilibrium between the outlet gas and the outlet solid is attained. Moreover, the integral in the second line of Eq. (57) with $c = c_{\mathrm{s}}$ describes the associated entropy production per unit mass of the controlled solid. Indeed, for the "workless" HFE process we find

$$\begin{aligned} S_{\sigma} &= \int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} \left(\frac{1}{T}-\frac{1}{T'}\right)\mathrm{d}Q_{\mathrm{s}} \\ &= \int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} c_{\mathrm{g}}\left(\frac{1}{T}-\frac{1}{T'}\right)(T'-T)\,\mathrm{d}G_{\mathrm{g}}/G_{\mathrm{s}} \\ &= \int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}} c_{\mathrm{s}}\frac{(T'-T)}{T'T}\,\mathrm{d}\tau. \end{aligned} \quad (60)$$

Thus the purely dissipative process of fluidized heat exchange can model 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 model and 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 approach referring to continuous processes in a horizontal fluidized heat exchanger will be extended to HFE dryers of this sort. These continuous systems are limiting configurations for cascades of fluidized heat exchangers and dryers. (Counterparts of resulting expressions for cascades with finite number of stages are derivable in a straightforward way: integrals are replaced by corresponding sums.)

8. Final remarks

We are now prepared to formulate a few basic conclusions. Heat exchange operations can be conducted conventionally, in traditional heat exchangers, or in a work-assisted way with heat-mechanical operations. The analysis of the derived optimization models for traditional and work-assisted operations shows that a useful parallelism is operative for expressions describing entropy sources, exergy costs and kinetic equations in both sorts of operations. This parallelism is particularly lucid in the realm of processes with pure heat transfer in which a special control variable T', called the Carnot temperature, is essential. In the second part of this work the parallelism is generalized to include coupled processes (those with simultaneous heat and mass transfer) in which case the operational models apply the suitable Carnot potentials $-1/T'$ and μ'/T'. Due to the parallelism, the mathematical identity does exist between expressions that link work and entropy production through the Gouy–Stodola law in traditional and work-assisted operations. With the process representation in terms of Carnot intensities we achieve the coincidence of the entropy production expressions in conventional and work-assisted operations. Eq. (60) thus applies for heat-mechanical processes as representations of their lost work divided by T^{e}. This is important; up to now it was unknown whether an equation of the classical structure could serve as a sufficiently exact model for a work-assisted system. Discovery of the Carnot controls was the necessary fact to prove the equivalence of mathematical models for both sorts of operations. The benefit from the described parallelism is that expressions for exergy losses in traditional coupled exchangers (without work production) can model exergy losses in more complex operations, those in heat-mechanical processes. Both multistage processes (described by difference equations and optimization criteria in the form of sums) and corresponding continuous processes (described by differential equations and optimization criteria in the form of integrals) can be modelled.

Within the thermodynamic theory of non-Carnot efficiencies for multistage heat-mechanical operations with heat conducting fluids, we have shown how to obtain suitable optimization criteria whose optimal values describe the work limits. We have applied the discovered parallelism between the work-assisted and traditional operations to obtain the work limits for finite-time sequences. The potential functions, obtained via optimization, define bounds on work consumption or production in heat-mechanical operations. For short durations, the consumption (lower) bound is significantly higher than the minimal work of classical thermodynamics; the production (upper) bound can be much lower. In particular these effects are associated with an increase of real work in energy utilization operations requiring only finite amount of time.

We also stress the observation that even the non-Newtonian nature of heat 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 media may exhibit complex non-Newtonian properties, the method is capable of evaluating energy limits in arbitrarily complex systems (with, e.g., dried bodies, radiation fluids, polymers, etc.). Some of these applications are reported in Part II of this paper.

Acknowledgements

Prof. Jan Szargut of Silesian University (Gliwice, Poland) has kindly sent the reprints of his papers to one of the authors (S.S.) thus enabling their evaluation here. The critical aspects of this evaluation are solely the responsibility of the first author (S. Sieniutycz).

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