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Article

An Unified Approach to Limits on Power Generation and Power Consumption in Thermo-Electro-Chemical Systems

Stanisław Sieniutycz

Faculty of Chemical and Process Engineering, Warsaw University of Technology, Waryńskiego Street No. 1, Warsaw 00-645, Poland; E-Mail: sieniutycz@ichip.pw.edu.pl

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Abstract: This research presents a unified approach to power limits in power producing and power consuming systems, in particular those using renewable resources. As a benchmark system which generates or consumes power, a well-known standardized arrangement is considered, in which two different reservoirs are separated by an engine or a heat pump. Either of these units is located between a resource fluid ('upper' fluid 1) and the environmental fluid ('lower' fluid, 2). Power yield or power consumption is determined in terms of conductivities, reservoir temperatures and internal irreversibility coefficient, Φ. While bulk temperatures T_i of reservoirs' are the only necessary state coordinates describing purely thermal units, in chemical (electrochemical) engines, heat pumps or separators it is necessary to use both temperatures and chemical potentials μ_k. Methods of mathematical programming and dynamic optimization are applied to determine limits on power yield or power consumption in various energy systems, such as thermal engines, heat pumps, solar dryers, electrolysers, fuel cells, *etc*. Methodological similarities when treating power limits in engines, separators, and heat pumps are shown. Numerical approaches to multistage systems are based on methods of dynamic programming (DP) or on Pontryagin's maximum principle. The first method searches for properties of optimal work and is limited to systems with low dimensionality of state vector, whereas the second investigates properties of differential (canonical) equations derived from the process Hamiltonian. A relatively unknown symmetry in behaviour of power producers (engines) and power consumers is enunciated in this paper. An approximate evaluation shows that, at least ¼ of power dissipated in the natural transfer process must be added to a separator or a heat pump in order to assure a required process rate. Applications focus on drying systems which, by nature, require a large amount of thermal or solar energy. We search for minimum power consumed in one-stage and multi-stage operation of fluidized drying. This multi-stage system is supported by heat pumps. We outline the related dynamic programming procedure, and also point out a link between the present irreversible approach and the classical problem of minimum reversible work driving the system.

Keywords: engines; heat pumps; separators; dryers; solar energy; power limits; energy consumption

Nomenclature

a	temperature exponent in an exchange equation [-]
$a_0 = 4\sigma/c$	radiation constant related to the Stefan-Boltzmann constant [$\mathrm{J\ m^{-3}K^{-4}}$]
a_v	exchange area per unit volume [$\mathrm{m^{-1}}$]
E^0, E_0	Nernst and idle run voltages [V]
$\dot{G}$	resource flux [$\mathrm{g\ s^{-1}}$], [$\mathrm{mols^{-1}}$]
g_1, g	partial and overall conductance [$\mathrm{J\ s^{-1}K^{-a}}$]
f_0, f_i	profit rate and process rates [-]
H, $\widetilde{H}$	standard and enlarged Hamiltonian functions
H_{TU}	height of transfer unit [m]
h	numerical value of Hamiltonian [$\mathrm{J\ m^3K^{-1}}$]
h, h_v	specific and volumetric enthalpies [$\mathrm{J\ g^{-1}}$, $\mathrm{J\ m^{-3}}$]
$\widetilde{\mathbf{I}}$	current vector, Equation (39)
i	electric current density [$\mathrm{A\ m^{-2}}$]
n	flux of fuel reagents [$\mathrm{g\ s^{-1}}$, $\mathrm{mols^{-1}}$]
$p = \dot{W}$	power output [$\mathrm{J\ s^{-1}}$]
p_m^0	molar constant of photons density [$\mathrm{mol\ m^{-2}K^{-3}s^{-1}}$]
q	heat flux between a stream and power generator [$\mathrm{J\ s^{-1}}$]
Q	total heat flux involving transferred entropies [$\mathrm{J\ s^{-1}}$]
$\widetilde{\mathbf{R}}$	resistance tensor, Equation (39)
S, S_σ	entropy and entropy produced [$\mathrm{J\ K^{-1}}$]
s, s_v	specific and volumetric entropy [$\mathrm{J\ K^{-1}g^{-1}}$, $\mathrm{J\ K^{-1}m^{-3}}$]
$\mathbf{T}$	vector transformation function
T	variable temperature of resource [K]
T_1, T_2	bulk temperatures of reservoirs 1 and 2 [K]
$T_{1'}$, $T_{2'}$	temperatures of circulating fluid (Figure 2) K
T^e	temperature of the environment [K]
T'	Carnot temperature control [K]
$\dot{T} = u$	rate of control of T in non-dimensional time [K]
t	time, holdup time [s]
u and υ	rate controls, $dT/d\tau$ and dT/dt [K, $\mathrm{K\ s^{-1}}$]
V	voltage, maximum work function, respectively [V, $\mathrm{J\ mol^{-1}}$]
v	velocity of resource stream [$\mathrm{m\ s^{-1}}$]
W	work produced, positive in engine mode [J]
w	specific work at flow or power per unit molar flux [$\mathrm{J\ mol^{-1}}$]
X,Y	absolute moisture content and humidity in solid and gas phase, respectively (Figures 6–8)
x	mass fraction [-]
z	adjoint variable [-]

Greek Symbols

α_1, α'	partial and overall heat coefficients referred to respective cross-sections [J $m^{-2}s^{-1}K^{-1}$]
β	coefficient of radiation transfer related to molar constant of photons density p_m^0 and Stefan-Boltzmann constant; $\beta = \sigma a_v c_h^{-1}(p_m^0)^{-1}$ [s^{-1}]
ε	total energy flux, conservative along a conductor [J s^{-1}]
$\eta = p/q_1$	first-law thermal efficiency [-]
$\chi = \rho c_v(\alpha' a_v)^{-1}$	time constant assuring the identity of ratio t/χ with number of transfer units [s]
μ	chemical potential [J mol^{-1}]
μ'	Carnot chemical potential [J mol^{-1}]
Φ	factor of internal irreversibility [-]
ϕ	electric potential [V]
σ	Stefan-Boltzmann constant for radiation [J m^{-2} $s^{-1}K^{-4}$]
σ_s	entropy production of the system [J $K^{-1}s^{-1}$]
ξ	intensity index [-]
ζ	chemical efficiency [-]
τ	dimensionless time or number of transfer units [-]

Subscripts

C	Carnot point
g	gas
m	molar flow
s	entropy, solid
v	per unit volume
1,2	bulks of first and second fluid
1',2'	circulating fluid
0	idle run voltage

Superscripts

e	environment
i	initial state
f	initial state
0	ideal (equilibrium) voltage
‘	Carnot state

Abbreviations

CNCA: Chambadal-Novikov-Curzon-Ahlborn engine; DP: Dynamic Programming; HJB: Hamilton-Jacobi-Bellman equation

1. Introduction

Power limits are evaluated for both energy-producing and energy-consuming systems. In general these limits are determined by involved optimization methods in which total power yield is extremized with respect to process controls. In this paper we focus on a synthesis of limiting properties of energy-production and energy-consumption units, which means that upper limits of power released from engines are confronted with lower limits of power supplied to various "energy consumers" (heat pumps, separators, electrolysers, *etc*.). Classical methods of differential calculus and Lagrange multipliers are usually sufficient to determine power limits in steady systems. Yet, for dynamical systems, which are described by differential optimization models, the determining of power limits is generally a difficult task. Functionals of total power must be extremized (minimized for power consumers) by variational methods.

Systems producing energy (engines) and those consuming energy are usually treated separately in the literature. In comparison with the previous publications, discussed below, a novel point of the present paper is the enuntiation of certain, relatively unknown, symmetry in behavior of energy consumers and energy producers (engines). The development of the Hamiltonian treatment with complementary use of Bellman's dynamic programming (DP) offers for dynamical processes a synthesizing treatment seldom applied in previous publications [1–5]. Not in order Discrete difference equations are derived here as canonical equations for the process Hamiltonian, and solved by numerical methods. Therefore the "curse of dimensionality" observed for the DP algorithms is avoided. Pontryagin's type (Hamiltonian-based) approaches [6–12], are outlined in Section 5. Yet, the DP approaches remain useful, especially when investigating properties of extremal costs. In fact, the simultaneous use of both methods is sometimes quite reasonable. Finally, the novelty of the paper lies in its generalizing formalism, which offers a synthesizing thermodynamic model to treat various energy generators (engines) and energy consumers (thermal, radiative, and electrochemical).

The inclusion of electrolysers into the family of separators, while quite natural, is original and beneficial to the theory of fuel cell systems that have recently attracted many researchers. The limitation of the approach is manifested, however, whenever the FC topology differs from that of the thermal or chemical system.

The length limitation of the present paper does not allow for inclusion of all derivations to make the paper self-contained, thus the reader may need to turn to some previous works [1–3,13,14]. In particular we must relegate to the Appendix derivations of special while very useful control variables (Carnot controls [1,13]). This Appendix generalizes the theory of thermal systems (with temperatures of circulating fluid $T_{1'}$ and $T_{2'}$; Chapter 3 of ref. [13]) for the case of chemical systems. In the main text the ideas referring to endoreversible systems are generalized to those with internal dissipation.

2. Steady Thermal Systems with Internal Dissipation

A great deal of research on power limits published to date considers stationary systems, in which case both reservoirs are infinite. Consider, for instance, steady-state analyses of the Chambadal-Novikov-Curzon-Ahlborn engine (CNCA engine [1,13,14]), in which the energy exchange is described by Newtonian law of cooling, or the Stefan-Boltzmann engine: a system with two radiation fluids and the energy exchange governed by the Stefan-Boltzmann law [15]. Because of their stationarity (caused by the infiniteness of each reservoir), the power maximizing controls are lumped to a fixed point in the state space. For a CNCA engine, the maximum power point may be related to the optimum value of a free (unconstrained) control variable, which can be efficiency η or Carnot temperature T'. The text below summarizes basic results in this field obtained for systems with internal dissipation (irreversibility factor Φ).

For a stationary heat operation of CNCA type [1,13,14], with bulk temperatures T_1 and T_2 and internal irreversibility factor Φ, the propelling heat in terms of Carnot temperature is [1,13]:

$$q_1 = g(T_1, T_2, \Phi)(T_1 - T') \tag{1}$$

where g is an effective overall conductance which may be the function of bulk state and Φ. Hence the power output is:

$$p = g(T_1, T_2, \Phi)(1 - \frac{\Phi T_2}{T'})(T_1 - T') \tag{2}$$

Setting to zero the partial derivative of p with respect to T' one finds at the maximum power point:

$$T'_{opt} = (T_1 \Phi T_2)^{1/2} \tag{3}$$

Since the effective environment temperature equals ΦT_2 and the Carnot structure holds for thermal efficiency η in terms of Carnot T', the power-maximizing efficiency follows as:

$$\eta_{mp} = 1 - \Phi T_2 / T'_{opt} = 1 - \sqrt{\Phi T_2 / T_1} \tag{4}$$

This equation represents a generalization of the classical CNCA formula whenever internal imperfections (coefficient Φ) are essential in the heat power system.

For the Stefan-Boltzmann engine an exact expression at the optimal power point cannot be determined analytically, yet, the temperature can be found graphically from the chart p = f(T'). A pseudo-Newtonian model [4,15,16], which treats state dependent energy exchange with coefficient $\alpha(T^3)$, omits to a considerable extent analytical difficulties of the Stefan-Boltzmann equation. Moreover, we can extend the present approach to dynamical systems, as outlined in the next section.

As shown in Appendix Equation (A19), total entropy production of the endoreversible power generation by the simple reaction $A_1 - A_2 = 0$ (isomerisation or phase change of A_1 into A_2), takes the following form:

$$\sigma_s = \varepsilon_1 (\frac{1}{T'} - \frac{1}{T_1}) + (\frac{\mu_1}{T_1} - \frac{\mu'}{T'}) n_1 \tag{5}$$

where $\varepsilon = q + h_a n_a + h_b n_b .... + h_k n_k$ is total energy flux in state 1 (driving the process). Decrease of efficiency in endoreversible engines, heat pumps and drying separators is the consequence of external irreversibilities quantified by the above expression.

When internal irreversibilities are essential, the imperfection factor Φ should be included in the considered expression according to the substitution rules:

$$\frac{\Phi}{T'} \text{ in place of } \frac{1}{T'} \text{ and } \frac{\Phi \mu'}{T'} \text{ in place of } \frac{\mu'}{T'}$$

as shown in [1], Equation (4.20) therein.

3. Some Results for Dynamical Thermal Systems

In the considered case, power maximization problem requires the use of variational metods (to handle extrema of functionals) in place of static optimization methods (which handle extrema of functions). The obtained non-exponential shape of the relaxation curve is the consequence of nonlinear properties of a driving fluid (e.g., radiation fluid). Non-exponential are also other curves describing the radiation relaxation, e.g., those based on the Stefan-Boltzmann equation [4,15–17]. A discrete model, involving difference equations, is usually used for calculation of a dynamical engine.

The dynamical energy yield, Figures 1 and 2, is connected with a limited amount of the resource fluid. The operation may be viewed as the sequence of small elementary engines of CNCA type, *i.e.*, the sequence of small units shown in Figure 1. In a thermal engine this mode of power yield involves the continual decrease of the resource temperature $T_1 = T(t)$ (approximated here by the sequence T^n). The optimization procedure searches for an extremal curve rather than an extremum point.

Figure 1. A scheme of a multistage control with distinguished time interval, Θ^n. When the method of the dynamic programming is applied, in the forward algorithm, elipse-shaped balance areas pertain to sequential subprocesses which grow by inclusion of following units in the way described by Bellman's recurrence equation. When algorithms of Pontryagin's type are applied, the optimal evolution is characterized by the difference canonical equations and extremum conditions of the Hamiltonian H^n with respect to controls.

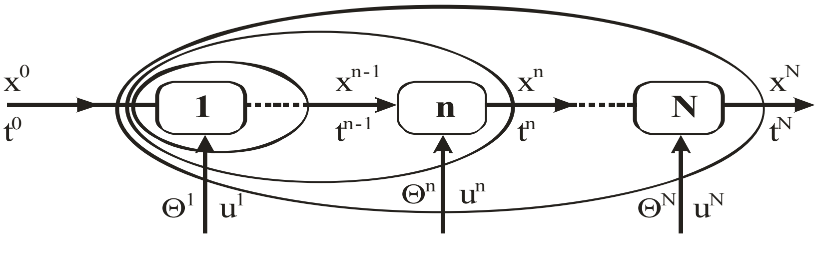
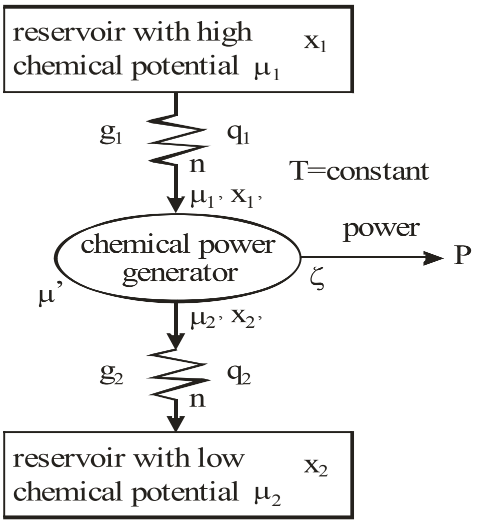


Figure 2. Principle of a steady thermo-chemical engine driven by heat and mass transfer.



Power maximizing $T(t)$ is accompanied by optimal control $T'(t)$; they are both components of the dynamical solution which satisfies a Hamilton-Jacobi-Bellman equation (HJB equation) for the optimal control. Expressions extremized in HJB equations of dynamical power problems are Hamiltonians, H. With a feedback control, the optimal temperature T' is obtained as the quantity maximizing H with respect to Carnot temperature at each point of the path.

For example, by applying the pseudo-Newtonian model, we obtain an optimal dynamics of relaxing radiation in the form:

$$\dot{T} = \xi(h_\sigma, T, \Phi)T \ . \tag{6}$$

Equation (6) describes the optimal trajectory in terms of state T and constant h_σ which is a constant numerical value of H along an optimal path. The related optimal Carnot control has the structure:

$$T' = \left(1 + \xi(h_\sigma, \Phi, T)\right)T \tag{7}$$

Compared with linear systems, the pseudo-Newtonian relaxation curve is not exponential. When standard boundary conditions for exergy are used, optimal work functions become generalized (rate dependent) exergies [1,13]. A more exact approach to radiation engines, described below, abandons the pseudo-Newtonian approximation and uses the exact Stefan-Boltzmann equations from the beginning.

4. Radiation Engines Decribed by the Stefan-Boltzmann Equations

In the dynamical radiation engines at least one reservoir is finite. The power integral involves the product of differential heat and imperfect efficiency [1,4,13]:

$$\dot{W} = \int -\dot{G}_c\left(1 - \frac{\Phi T^e}{T'}\right)dT \tag{8}$$

When the propelling medium consists of the radiation fluid, power maximization problem is described by Equations (8) and (9) below. They describe a *symmetric model of power yield from radiation* (both reservoirs consist of radiation). In the physical space, power exponent $a = 4$ for radiation and $a = 1$ for a linear resource. The integrand of Equation (8) represents power intensity as the intensity of a generalized profit, f_0.

In the engine mode, integral (8) has to be maximized, subject to the dynamical constraint ('state equation') derived in recent publications [4,15,16]:

$$\frac{dT}{dt} = -\beta\frac{T^a - T'^a}{(\Phi'(T'/T^e)^{a-1} + 1)T^{a-1}} \tag{9}$$

As it follows from the general theory of dynamic optimization, extremum conditions for the problem involving Equations (8) and (9) are contained in the HJB equation of the problem:

$$\frac{\partial V}{\partial t} - \max_{T'(t)}\left\{\left(\dot{G}_c(T)\left(1 - \Phi'\frac{T^e}{T'}\right) + \frac{\partial V}{\partial T}\right)\beta\frac{T^a - T'^a}{(\Phi'(T'/T^e)^{a-1} + 1)T^{a-1}}\right\} = 0 \tag{10}$$

where $V = \max\dot{W}$. Since the equation above cannot be solved analytically, except for the case when $a = 1$, a numerical solution can be pursued, based on Bellman's method of dynamic programming (DP).

Taking into account computational needs, discrete difference equations are derived, and solved by numerical methods. Thus we introduce a related discrete scheme:

$$\dot{W}^N = \sum_{k=1}^{N} -\dot{G}_c(T^k).\left(1 - \frac{\Phi T^e}{T'^k}\right)(T^k - T^{k-1}) \tag{11}$$

$$T^k - T^{k-1} = \theta^k\beta\frac{{T'^k}^a - {T^k}^a}{(\Phi'(T'^k/T^e)^{a-1} + 1){T^k}^{a-1}} \tag{12}$$

$$t^k - t^{k-1} = \theta^k \tag{13}$$

An optimizer searches for a maximum of the sum (11) subject to discrete constraints (12) and (13). Applying to this problem the dynamic programming method, the following recurrence equation is obtained for the minimum power function $R = \min(-\dot{W})$:

$$R^n(T^n,t^n) = \min_{u^n,\theta^n}\left\{\dot{G}_c(T^n).\left(1-\frac{\Phi T^e}{T'^n}\right)\beta\frac{T^{na}-T'^{na}}{(\Phi'(T'^n/T^e)^{a-1}+1)T'^{na-1}}\theta^n + R^{n-1}\left((T^n-\frac{\theta^n\beta(T'^{na}-T^{na})}{[\Phi'(T'^n/T^e)^{a-1}+1]T'^{na-1}},t^n-\theta^n\right)\right\} \tag{14}$$

While the analytical treatment of Equations (8) and (9) is a formidable task, it is quite easy to solve recurrence Equation (14) numerically. Low dimensionality of state vector in Equation (14) assures a good accuracy of DP solution. Moreover, an original accuracy can be improved after performing the so-called dimensionality reduction associated with the elimination of time variable t^n. In the transformed problem, without t^n, accuracy of DP solutions is high.

However, when the number of state variables increases (e.g., when several concentrations x_i^n accompany temperature T^n as in chemical engines), DP algorithms become inefficient and inaccurate. We must then abandon DP approaches and turn to the Pontryagin type (Hamiltonian-based) approaches. For the Hamiltonian approaches, which apply Pontryagin's canonical equations, problems of large dimensionality of state vectors are inessential, as outlined in the section below.

5. Hamiltonian-Based Approaches

The dynamic changes for the discrete state of a multistage system can be described by a set of ordinary difference equations called state transformations which describe the discrete state from the stage $n-1$ in terms of the state from the stage n and some control variables U^n.

The set of discrete state transformations can be written in the following general form:

$$\boldsymbol{x}^{n-1} = \boldsymbol{T}^n\left(\boldsymbol{x}^n, t^n, \boldsymbol{U}^n\right) \tag{15}$$

where:

$$t^n = t^{n-1} + \theta^n \tag{16}$$

and, $\boldsymbol{U}^n = \left(\boldsymbol{u}^n, \theta^n\right)$ is an enlarged vector of control variables which includes the discrete interval of time θ^n, and the time variable t^n is identified with any state variable growing monotonically. After defining the function:

$$\mathbf{f}^n = (\mathbf{x}^n - \mathbf{T}^n(\mathbf{x}^n, t^n, \mathbf{U}^n))/\theta^n \tag{17}$$

the above state transformations can be given the form of discrete state equations [17,18]:

$$\mathbf{x}^{n-1} = \mathbf{x}^n - \mathbf{f}^n(\mathbf{x}^n, t^n, \mathbf{u}^n, \theta^n)\theta^n \tag{18}$$

and:

$$t^{n-1} = t^n - \theta^n \tag{19}$$

Since they involve the discrete rates (f^n, 1), we call this form the "standard form".

A performance index describing a generalized profit (total power in our case) is defined by the following equation:

$$P^N \equiv \dot{W}^N = \sum_{n=1}^{N} f_0^n(\mathbf{x}^n, t^n, \mathbf{u}^n, \theta^n)\theta^n \tag{20}$$

where f_0 is a generation rate for the generalized profit (power in the case of energy yield problems).

To solve the optimization problem of extremum W, an enlarged (time-constraint absorbing) Hamiltonian is defined in the following form:

$$\begin{aligned}&\widetilde{H}^{n-1}(\mathbf{x}^n, t^n, \mathbf{z}^{n-1}, \mathbf{u}^n, \theta^n) \equiv \\ &f_0^n(\mathbf{x}^n, t^n, \mathbf{u}^n, \theta^n) + \sum_{i=1}^{s} z_i^{n-1} f_i^n(\mathbf{x}^n, t^n, \mathbf{u}^n, \theta^n) + z_t^{n-1} \equiv H^{n-1} + z_t^{n-1}\end{aligned} \tag{21}$$

where z_i are adjoint (Pontryagin's) variables.

In an optimal process the enlarged Hamiltonian $\widetilde{H}^{n-1}$ satisfies in the enlarged phase space $x = (\mathbf{x}, t)$ and $z = (\mathbf{z}, \mathrm{z}_t)$ the following equations:

$$\frac{x_i^n - x_i^{n-1}}{\theta^n} = \frac{\partial \widetilde{H}^{n-1}}{\partial z_i^{n-1}} \tag{22}$$

(state equations) and:

$$\frac{z_i^n - z_i^{n-1}}{\theta^n} = -\frac{\partial \widetilde{H}^{n-1}}{\partial x_i^n} \tag{23}$$

(adjoint equations), and the equations which describe the necessary optimality conditions for decision variables $\mathbf{u}^n$. For example, if the optimal control lies within an interior of admissible control set:

$$\partial[\theta^n \widetilde{H}^{n-1}(\boldsymbol{x}^n, z^{n-1}, \theta^n, \mathbf{u}^n)]/\partial\theta^n = 0 \tag{24}$$

and:

$$\frac{\partial \widetilde{H}^{n-1}}{\partial u_j^n} = 0 \tag{25}$$

Equation (24) implies the vanishing of the enlarged Hamiltonian $\widetilde{H}^{n-1}$ along a discrete optimal path whenever discrete rates f_i are independent of θ^n. In addition, the energy-like Hamiltonian (without z_t term) is constant for the process whose rates are independent of time t^n. Under convexity properties for rate functions and constraining sets the optimal controls are defined by the equations:

$$\theta^n = \underset{\theta^n}{\arg\max}\{\theta^n \widetilde{H}^{n-1}(\mathbf{x}^n, z^{n-1}, \mathbf{u}^n, \theta^n)\} \tag{26}$$

and:

$$\mathbf{u}^n = \underset{\mathbf{u}^n}{\arg\max}\{\widetilde{H}^{n-1}(\mathbf{x}^n, z^{n-1}, \mathbf{u}^n, \theta^n)\} \tag{27}$$

(n = 1,...N; i = 1,...s+1 and j = 1,...r.)

Optimization theory for generalized (θ^n -dependent) costs and rates provides a bridge between constant-H algorithms [5,19,20] and more conventional ones such as those by Katz [21], Halkin [6], Canon *et al.* [7], Boltyanskii [8], and many others [9,18]. Since, as shown by Equation (24), control θ^n can be included in the Hamiltonian definition, *i.e.*, an effective Hamiltonian can be used:

$$\mathsf{H}^{\mathrm{n}-1} = \widetilde{H}^{n-1}\theta^\mathrm{n}, \tag{28}$$

extremum conditions (22)–(27) can be written in terms of $\mathsf{H}^{\mathrm{n}-1}$. The related canonical set is that of Halkin [6,7]:

$$x_i^n - x_i^{n-1} = \frac{\partial \mathrm{H}^{n-1}}{\partial z_i^{n-1}} \tag{29}$$

$$z_i^n - z_i^{n-1} = -\frac{\partial \mathrm{H}^{n-1}}{\partial x_i^n} \tag{30}$$

Qualitative difference between the role of controls u^n and θ^n in the optimization algorithm is then lost since they both follow from the same stationarity condition for Hamiltonian H^{n-1} in an optimal process. For example, in the weak maximum principle:

$$\frac{\partial \mathrm{H}^{n-1}}{\partial \theta^n} = \frac{\partial \mathrm{H}^{n-1}}{\partial u_j^n} = 0 \tag{31}$$

in agreement with Equations (24) and (25) above. Moreover, for the enlarged Hamiltonian $\tilde{H}^{n-1}$, Equations (24), (28) and (31) imply the condition $\tilde{H}^{n-1} = 0$ if $\tilde{H}^{n-1}$ is independent of time interval θ.

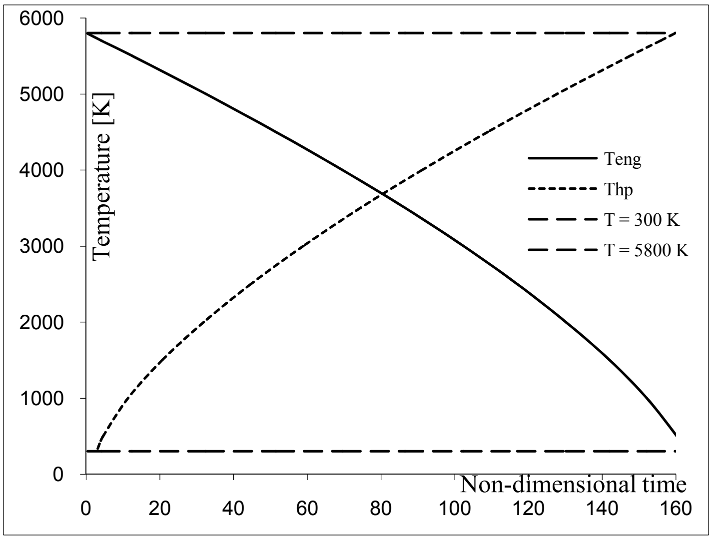
Until recently, Hamiltonian algorithms were used in power systems for models with θ- independent discrete rates [10]. Poświata and Szwast have shown many their applications in exergy optimization of thermal and separation systems, in particular fluidized dryers [11,12,17]. Sieniutycz has shown some other applications for energy and separation systems and for a minimum time problem [18]. Taking into account the diversity of discrete rates, which may contain explicit intervals θ^n as the consequence of various ways of discretizing, applications of algorithm (17)–(25) in power or separation systems are both appropriate and useful.

In particular, the algorithm is applicable in numerical studies of the optimal solutions for the discrete equations of the radiation engine, Equations (11)–(13), for which the enlarged Hamiltonian has the form:

$$\tilde{H}^{n-1} = \left(z_T^{n-1} - \dot{G}_c(T^n)\right)\left(1 - \frac{\Phi T^e}{T'^n}\right) \times \beta \frac{T^{n^a} - T'^{n^a}}{(\Phi'(T'^n/T^e)^{a-1} + 1)T^{n^{a-1}}} + z_t^{n-1} \tag{32}$$

Optimal dynamics corresponding to this function are shown in Figure 3.

Figure 3. Decreasing temperatures of radiation relaxing in engine mode and increasing temperature of radiation utilized in heat pump mode in terms of time, for a constant value of Hamiltonian $H = 1 \times 10^{-8}$ [J K^{-1}m^{-3}] [4].



6. Simple Chemical Systems

Thermodynamic approaches can also be applied to chemical [2,14] and electro-chemical [22,23] engines. In chemical engines mass transports drive transformation of chemical energy into mechanical power. In chemical machines, as opposed to thermal machines, generalized streams or reservoirs are present, capable of providing both heat and substance. Large streams or infinite reservoirs assure constancy of chemical potentials. Problems of maximum of power produced or minimum of power consumed are then the static problems. For a finite "upper stream", however, the amount and chemical potential of an active reactant decrease in time, and problems considered are those of dynamic optimization and variational calculus. Because of the diversity of chemical systems the area of power producing chemistries is quite broad.

Power expression and efficiency formula for a chemical system follow from the entropy conservation and energy balance in the power-producing zone of the system ('active part'). The simplest model of power producing chemical engine is that with an isothermal isomerization reaction, $A_1 - A_2=0$ [2,14]. In an 'endoreversible engine' total entropy flux is continuous through the active zone. When a formula describing this continuity is combined with an isothermal energy balance we find:

$$p = (\mu_{1'} - \mu_{2'})n_1 \tag{33}$$

where the feed flux n_1 equals to n, an invariant molar flux of reagents. Process efficiency ζ is defined as power yield per molar flux, n. This efficiency is identical with the chemical affinity of reaction in the chemically active part of the system. While ζ is not dimensionless, it describes correctly the system. In terms of Carnot variable, μ', which satisfies Equation (19) in the Appendix:

$$\zeta = \mu' - \mu_2 \tag{34}$$

For a steady engine the following function describes chemical Carnot control μ' in terms of fuel flux n_1 and its mole fraction x:

$$\mu' = \mu_2 + \zeta_0 + RT\ln\left(\frac{x_1 - n_1 g_1^{-1}}{n_1 g_2^{-1} + x_2}\right) \tag{35}$$

As Equation (34) is valid, Equation (35) also characterizes the efficiency control in terms of n and fuel fraction x. Equation (35) shows that an effective concentration of the reactant in upper reservoir $x_{1\text{eff}} = x_1 - g_1^{-1}n$ is decreased, whereas an effective concentration of the product in lower reservoir $x_{2\text{eff}} = x_2 + g_2^{-1}n$ is increased due to the finite mass flux. Therefore efficiency ζ decreases nonlinearly with n. When the effect of resistances is negligible or flux n is very small, reversible Carnot-like chemical efficiency, ζ_C, is attained. The power function, described by the product $\zeta(n)n$, exhibits a maximum for a finite value of the fuel flux, n.

A related dynamical problem may also be considered [3]. Application of Equation (35) to the Lagrangian relaxation path leads to a work functional:

$$W = -\int_{\tau_1^i}^{\tau_1^f} \left\{\zeta_0 + RT\ln\left(\frac{X/(1+X) + dX/d\tau_1}{x_2 - jdX/d\tau_1}\right)\right\}\frac{dX}{d\tau_1}d\tau_1 \tag{36}$$

whose maximum describes the dynamical limit of the system. Here X = x/(1 − x) and *j* equals the ratio of upper to lower mass conductance, g_1/g_2. The path optimality condition may be expressed in terms of the constancy of the following Hamiltonian:

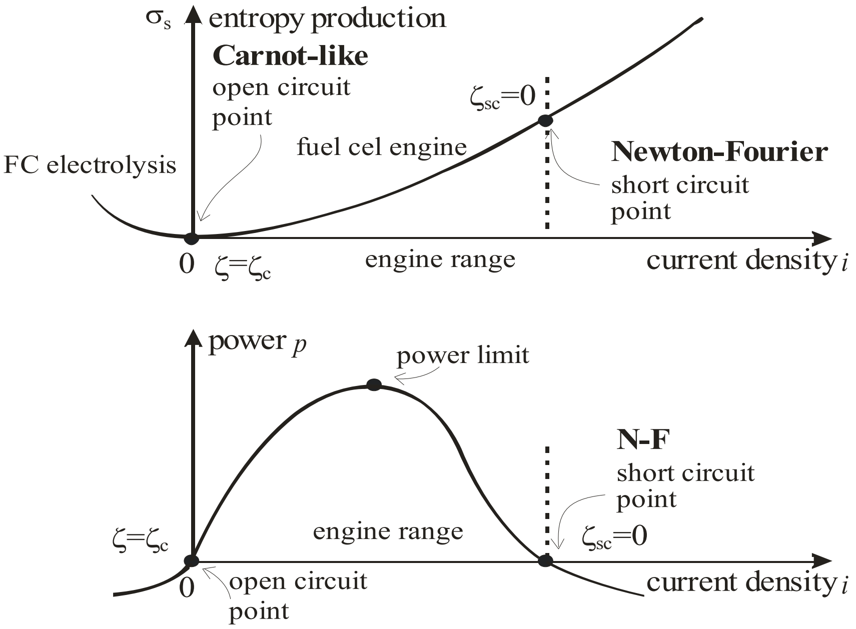
$$H(X,\dot{X}) = RT\dot{X}^2\left(\frac{1+X}{X}+\frac{j}{x_2}\right) \tag{37}$$

For low rates and large concentrations *X* (mole fractions x_1 close to the unity) optimal relaxation rate of the fuel resource is approximately constant. Yet, in an arbitrary situation optimal rates are state dependent so as to preserve constancy of *H* in Equation (37).

7. Power Limits in Fuel Cells

Fuel cells have attracted great attention by virtue of their inherently clean and reliable performance. Their main advantage as compared to heat engines is that their efficiency is not a major function of device size. A fuel cell is an electrochemical energy converter which directly and continuously transforms a part of chemical energy into electrical energy by consuming fuel and oxidant. Power maximization approaches can be applied to many electrochemical systems, in particular to fuel cells [22,23]. Power decrease below ideal (Nernst) value and power maxima in engines are associated with entropy production, Figure 4.

Figure 4. Entropy production and power yield in an electrochemical engine or fuel cell in terms of density of electric current.



Voltage lowering in fuel cells below the reversible value is a reasonable measure of their imperfection. Reversible cell voltage E^0 is often a reference basis calculated from the Nernst equation. Yet, in more general cases, actual voltage without load must take into account losses of the idle run, which are the effect of flaws in electrode constructions and other imperfections. In [23] and many other works the operating voltage of a cell is evaluated as the departure from the idle run voltage E_0:

$$V = E_0 - V_{\mathrm{int}} = E_0 - V_{\mathrm{act}} - V_{\mathrm{conc}} - V_{\mathrm{ohm}} \tag{38}$$

Losses, which are called polarization, include three main sources: activation polarization (V_{act}), ohmic polarization (V_{ohm}), and concentration polarization (V_{conc}). Power density is the product of voltage V and current density i. A large number of approaches for calculating polarization losses has been presented in literature, as reviewed in [22]. Experiments show power maxima in fuel cells [22,23]. Activation and concentration polarization occur at both anode and cathode locations. The resistive polarization represents ohmic losses throughout the cell. As the voltage losses increase with current, the initially increasing power begins finally to decrease for sufficiently large currents, so that maxima of power are observed [22,23]. The data include the losses of the idle run, attributed to flaws in electrode constructions and other imperfections.

Validation of the thermodynamic model of fuel cell is based on the application of the Aspen Plus$^{\mathrm{TM}}$ software for simulation purposes and organization of FC power experiments, as described in Wierzbicki's M.Sc thesis [23]. A complete review of the theory and experiments is presented in the report [24].

To quantify the power yield and power limits let us focus on fuel cells described by the formalism of inert components [25,26] rather than the ionic description [27]. Assume, for simplicity, that the active (power producing) driving forces involve only: one temperature difference $T_{1'} - T_{2'}$, single chemical affinity $\mu_{1'} - \mu_{2'}$ and the operating voltage $\phi_{1'} - \phi_{2'}$. Total power production is the sum of thermal, substantial and electric components, *i.e.*,:

$$\begin{aligned} P &= (T_{1'} - T_{2'})I_{\mathrm{s}} + (\mu_{1'} - \mu_{2'})I_{\mathrm{n}} + (\phi_{1'} - \phi_{2'})I_{\mathrm{e}} \\ &= (T_1 - T_2)I_{\mathrm{s}} + (\mu_1 - \mu_2)I_{\mathrm{n}} + (\phi_1 - \phi_2)I_{\mathrm{e}} \\ &- R_{\mathrm{ss}}I_s^2 - R_{\mathrm{nn}}I_n^2 - R_{\mathrm{ee}}I_e^2 - R_{\mathrm{sn}}I_sI_n - R_{\mathrm{se}}I_sI_e - R_{\mathrm{ne}}I_nI_e \end{aligned} \tag{39}$$

Equation (38) represents linear thermo-electro-chemical systems. Linear systems are those with constant (current independent or flux independent) resistances or conductances. They satisfy Ohm type or Onsager type laws linking thermodynamic fluxes and thermodynamic forces (dissipative driving forces which are represented by products $R_{ik}I_k$ in Equation (39)). While many fuel cell systems are nonlinear, *i.e.*, possess current dependent resistances, the dependence is often weak, so the linear model can be a good approximation. Below we develop a simple theory of power limits for these systems. Based on experiments, these power limits are exemplified in Figure 5.

After introducing the enlarged vector of all driving potentials $\tilde{\boldsymbol{\mu}} = (T, \mu, \phi)$, the flux vector $\tilde{\mathbf{I}}$ of all currents and the overall resistance tensor $\tilde{\mathbf{R}}$, Equation (39) can be written in a simple matrix-vector form:

$$P = (\tilde{\boldsymbol{\mu}}_1 - \tilde{\boldsymbol{\mu}}_2).\tilde{\mathbf{I}} - \tilde{\mathbf{R}} : \tilde{\mathbf{I}}\tilde{\mathbf{I}} \tag{40}$$

Maximum power corresponds with the vanishing of the partial derivative vector:

$$\partial P / \partial \tilde{\mathbf{I}} = \tilde{\boldsymbol{\mu}}_1 - \tilde{\boldsymbol{\mu}}_2 - 2\tilde{\mathbf{R}}.\tilde{\mathbf{I}} = 0 \tag{41}$$

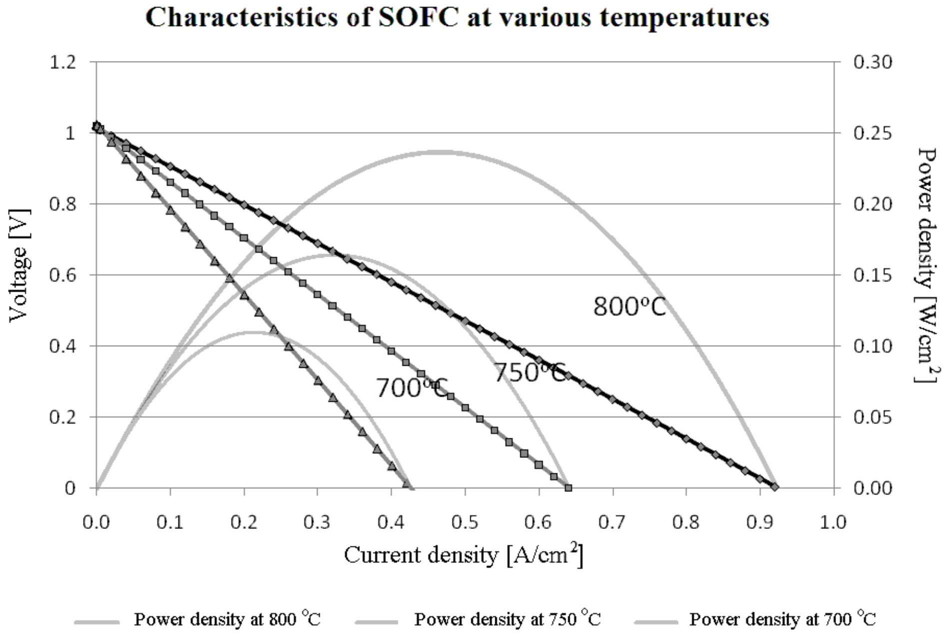
Consequently, the optimal (power-maximizing) vector of currents at the maximum point of the system can be written in the form:

$$\tilde{\mathbf{I}}_{mp} = \frac{1}{2}\tilde{\mathbf{R}}^{-1}.(\tilde{\boldsymbol{\mu}}_1 - \tilde{\boldsymbol{\mu}}_2) \equiv \frac{1}{2}\tilde{\mathbf{I}}_F \tag{42}$$

This result means that the power-maximizing current vector $\tilde{\mathbf{I}}_{mp}$ in strictly linear systems equals one half of the purely dissipative current at the Fourier-Onsager point, $\tilde{\mathbf{I}}_F$ at which no power production occurs. Moreover, we note that Equations (40) and (42) yield the following result for the maximum power limit of the system:

$$P_{mp} = \frac{1}{4}(\tilde{\boldsymbol{\mu}}_1 - \tilde{\boldsymbol{\mu}}_2).\tilde{\mathbf{R}}^{-1}.(\tilde{\boldsymbol{\mu}}_1 - \tilde{\boldsymbol{\mu}}_2) \tag{43}$$

Figure 5. Experimental voltage-current density and power-current density characteristics of the SOFC for various temperatures. Continuous lines represent the Aspen Plus^{TM} calculations testing the model versus the experiments. The lines were obtained in Wierzbicki's M.Sc thesis supervised by S. Sieniutycz and J. Jewulski [8]. Points refer to experiments of Wierzbicki and Jewulski in Warsaw Institute of Energetics (Wierzbicki [8], and his ref. [9]).



In terms of the purely dissipative flux vector at the Fourier-Onsager point, $\tilde{\mathbf{I}}_F$ the above limit of maximum power is represented by an equation:

$$P_{mp} = \frac{1}{4}\tilde{\mathbf{R}} : \tilde{\mathbf{I}}_F \tilde{\mathbf{I}}_F \tag{44}$$

Of course, the power dissipated at the Fourier-Onsager point equals:

$$P_F = \tilde{\mathbf{R}} : \tilde{\mathbf{I}}_F \tilde{\mathbf{I}}_F \tag{45}$$

Equations (44) and (45) prove that only at most 25% of power (45), which is dissipated in the natural transfer process, can be transformed into the noble form of the mechanical power. This result holds for linear systems, and, probably, cannot be easily generalized to the nonlinear transfer systems where significant deviations from Equation (44) are expected depending on the nature of diverse nonlinearities. Despite of the limitation of the result (44) to linear transfer systems its value is significant because it shows explicitly the order of magnitude of thermodynamic limitations in power production systems.

The above analysis also proves that a link exists between the mathematics of the thermal engines and fuel cells, and also that the theory of fuel cells can be unified with the theory of thermal and chemical engines.

A word of explanation of related physical effects is in order. While power ratios involving Equations (44) and (45) can be regarded as efficiency measures, they should not be mixed with commonly used, popular efficiencies, especially with first law efficiencies. In fact, the considered power ratios represent some specific, second-law efficiencies of the overall thermo-electro-chemical process. There is a number of definitions of FC efficiencies, based on first or second laws, proposed for measuring and comparing the performance of electrochemical processes. Only second-law efficiencies are correct measures, which show how closely the process approaches a reversible process. Efficiencies based on the first law (often found in the literature) can generate efficiency values greater than 100% for certain systems depending on whether the change in entropy for the overall chemical reaction involved in the process is positive or negative. See, for example, paper [28] on various definitions of FC efficiencies.

The popular fuel cell efficiencies, $\eta_{FC} = \Delta G/\Delta H$ or $\eta_{FC} = -W/\Delta H$, which are commonly applied to many fuel cell systems, can easily achieve numerical values much higher than ¼ [power ratio of Equations (44) and (45)]. They are, however, first-law efficiencies defined in a different way than the power ratios P_{mp}/P_F satisfying Equations (44) and (45).

8. Power Consumption Limits in Thermochemical Systems

Heat pumps and HP-supported dryers are typical representatives of systems driven by the consumed power. Since the use of power and efficiency formulae derived from analyses of power generators can be extended to units which consume power, it is interesting to develop analyses for units such as thermal and solar heat pumps, drying separators and electrolyzers. A meaningful reduction of drying exergy could be achieved by the optimal control of many dryers; on average, the potential for exergy reduction is more than 20%. Some industrial data are, however, still reported in terms of energy (enthalpy) rather than exergy efficiency, and suffer from a lack of a strong link with well established kinetic models.

Awareness of limited energy supplies prompts a significant effort in developing recovery processes. Possible operations and design modifications involve waste heat recovery from solids, energy recuperation from gases, application of heat pumps for waste energy upgrading, recycling of exhausted drying agent, combinations of mechanical and thermal drying, and use of solar energy.

Application of optimal control principles to processes with consumption of mechanical energy gives a certain extra potential for improving their economy. Some of these processes use thermal separators and heat pumps. The heat pump is in principle the only device which would allow exploitation of low-exergy sources commonly available in nature and industry. Heat pumps increase driving energy by adding low-quality energy taken from a low-exergy source to obtain energy of high quality economically. Mathematical analyses of power-assisted processes lead to optimization-determined bounds on power input and exergy dissipation.

We consider an optimal operation with HP-supported drying. Our optimization example refers to a non-ideal fluidized drying in which one stage can be modeled in two ways (pseudo-homogeneous and non-homogeneous), as shown in Figure 6 below. Symbols X and Y in Figures 6 to 8 refer to absolute moisture content and absolute humidity in solid and gas phase, respectively.

Figure 6. Two ways of modeling of fluidized drying (Szwast [29] and Sieniutycz [20], case A, and Poświata [22,30,31], case B). The scheme allows a simultaneous treatment of the batch fluidization and the fluidization in a horizontal exchanger as the continuous limit of the cascade.

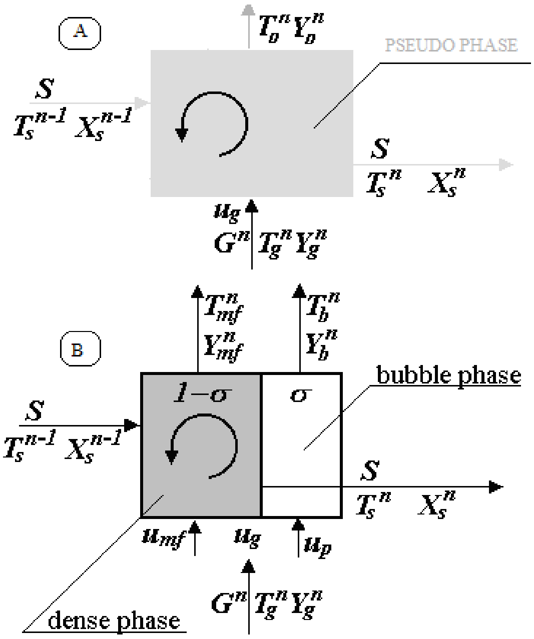


Figure 7. A scheme of one-stage drying operation with a heat pump 1 and a continuous co-current dryer D^1 with falling particles. The multistage idea means, of course, the repetition of this single-stage set in the next stages.

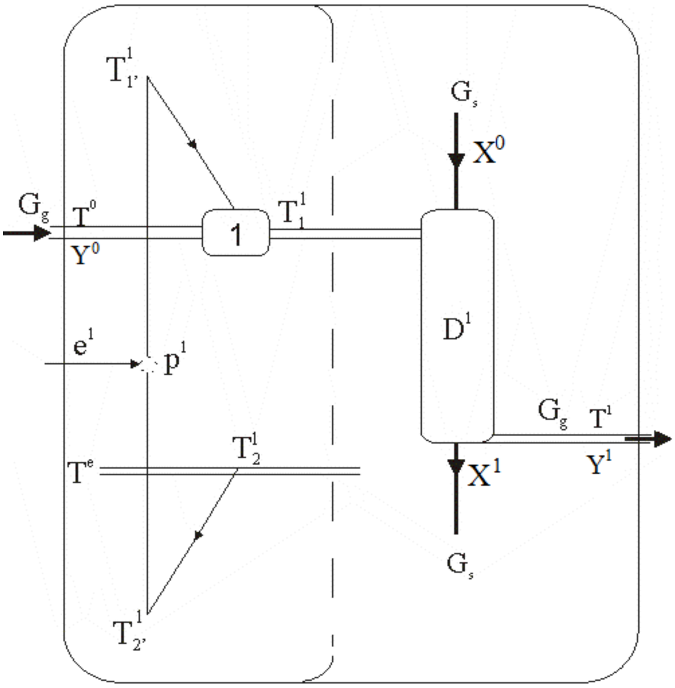
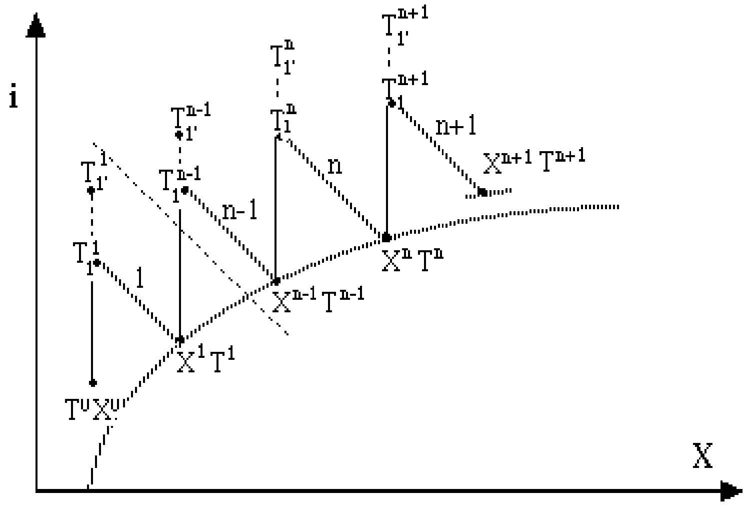


Figure 8. Changes of gas states in a multistage work-assisted drying operation on the gas enthalpy - gas humidity diagram, i-X. Primed states refer to temperatures of fluids circulating in the heat pumps which heat gases supplied to dryers 1, 2...n.



The multistage process is composed of several HP supported fluidized dryers, each drying process governed by the hydrodynamic model presented in Figure 6 and each stage characterized by Figure 7. The multistage idea involves, of course, the repetition of a single-stage operation in next stages. As a global effect, we achieve the operation shown in Figure 8 in which drying agents enter the dryer with suitably adjusted inlet states (with sufficiently high temperatures). Explicit input fluxes of mechanical power may be considered in these problems as possible controls.

In the considered power-assisted, multistage operation each drying agent is heated before each dryer by a heat pump, in order to achieve a sufficiently high temperature. This example involves a non-ideal fluidized drying in which one stage can be modeled in two ways (pseudo-homogeneous and non-homogeneous), Figure 6. In the multistage process the gas leaving the previous stage enters the heat pump and dryer of the next stage, Figure 7. For relatively efficient stages, we may assume that the outlet solid and gas are in the thermal equilibrium due to a large specific solid area. The properties of the heat pump as the heating device are important in this analysis; the better COP results in more efficient heating. The final effect is a complex process—in fact, a work-assisted drying operation—in which gas states vary as shown in Figure 8.

As shown in Figure 7 a stage of this complex multi-step operation comprises not a single dryer but rather an appropriate group of various units which is repeated when the process procedes from one step to another. This is a multi-stage drying operation, in which gas at each stage is first heated with a heat pump and then is directed to a dryer (note that only one stage of that operation is shown in Figure 7). In the considered case a continuous drying process occurs in a co-current dryer; yet the countercurrent contacting can alternatively be applied. The purpose is to minimize work consumption in, say, a two-stage operation by a suitable choice of the intermediate moisture content between the first and the second stage.

One may ask: how many heat pumps (and stages) are there in the optimal system? The answer is possible by making an economical analysis, and terminating the cascade calculations when the sum of operational and investment cost stops to decrease. As the investment cost grows steeply with the number of stages, the optimal number of stages is usually limited to a few stages.

The balances of mass and heat yield:

$$\frac{rG_s}{cG_g}(\mathsf{W}^0-\mathsf{W}^1)=(T_1^1-T^1), \tag{46}$$

$$T_1^1-T^1=-\frac{r}{c}(X_1^1-X_s(T^1)), \tag{47}$$

where r is evaporation heat of moisture and c is specific heat of gas. The power consumed at a single stage per unit flow of gas, e^1, is described by an expression [compare with Equation (8)]:

$$e^1\equiv-\frac{p}{G_g}=c\left(1-\frac{T^e}{T_1^1+u^1}\right)u^1\theta^1 \tag{48}$$

where u^1 is the energy supply to the drying gas in the condenser of the heat pump, and $u^1=-q^1/g>0$ is a measure of this energy supply in the temperature units. We may include the effect of internal irreversibilities within the heat pump in which case the performance coefficient of the support heat pump contains imperfection factor Φ as the multiplicative factor of the bath temperature T^e.

Substituting into Equation (48) the temperature T_1^1 following from transformed Equation (47):

$$T_1^1=T^1+\frac{r}{c}(X_s(T^1)-X_1^1) \tag{49}$$

and taking into account that $X_1^1=X^0$ [also $X_1^n=X^{n-1}=X_s(T^{n-1})$, for $n=2,..N$] we find the mechanical energy consumption at the stage:

$$e^1=c\left(1-\frac{T^e}{T^1+\frac{r}{c}(X_s(T^1)-X^0)+u^1}\right)u^1\theta^1 \tag{50}$$

Equation (50) is transformed further in view of the link between u^1 and θ^1 (consider difference constraint describing $\Delta T^n=u^n\theta^n$ for $n=1$):

$$e^1=c\left(1-\frac{T^e}{T^1+rc^{-1}(X_s(T^1)-X^0)+\dfrac{T^1+rc^{-1}(X_s(T^1)-X^0)-T^0}{\theta^1}}\right) \\ \times(T^1+rc^{-1}(X_s(T^1)-X^0)-T^0). \tag{51}$$

In terms of the 'adiabatic temperature function':

$$T^a(T^1)\equiv T^1+rc^{-1}X_s(T^1) \tag{52}$$

The work expression takes the final form:

$$e^1=c\left(1-\frac{T^e}{T^a(T^1)-rc^{-1}X^0+\dfrac{T^a(T^1)-rc^{-1}X^0-T^0}{\theta^1}}\right) \\ \times\left(T^a(T^1)-rc^{-1}X^0)-T^0\right). \tag{53}$$

An analogous function, but with the shifted superscripts, is valid for the second stage:

$$e^2 = c\left(1 - \frac{T^e}{T^a(T^2) - rc^{-1}X_s(T^1) + \dfrac{T^a(T^2) - rc^{-1}X_s(T^1) - T^1}{\theta^2}}\right) \times \left(T^a(T^2) - rc^{-1}X_s(T^1) - T^1\right) \tag{54}$$

The constraint $X^1 = X_S(T^1)$ resulting from the outlet phases equilibrium in the first dryer is incorporated in the second work expression. In terms of the adiabatic temperature at the second stage:

$$e^2 = c\left(1 - \frac{T^e}{T^a(T^2) - rc^{-1}X_s(T^1) + \dfrac{T^a(T^2) - T^a(T^1)}{\theta^2}}\right) \times \left(T^a(T^2) - T^a(T^1)\right) \tag{55}$$

The sum of both works yields the total work consumed. This total work is the thermodynamic cost that should be minimized. For a fixed holdup time $\tau^2 = \theta^1 + \theta^2$ there are two free controls: θ^1 and T^1. Thus we can accomplish the power minimization procedure.

The procedure searches for an optimal interstage temperature $T^1$and an optimal heat transfer area of the first heat pump a^1 present in the control variable θ^1. The requirement of sufficiently low final moisture content in a solid defines the amount of the evaporated moisture per unit time. The optimization can be generalized to the N-stage cascade system.

The example presented above shows how to optimize a drying operation with gas heated by a sequence of heat pumps. The optimization criterion is the power consumption, the optimal solution should assure the minimum of consumed power. The optimal transfer areas are close in value, the optimal temperatures constitute an increasing sequence. The optimal work supplied to the two-stage system decreases distinctly with the total transfer area.

A general thermokinetic theory of minimum power supply to power consumers can be developed, based on systems' thermodynamic and kinetic properties, as outlined below. Note a symmetry of this approach in relation to maximum power yield in power generators (fuel cells in Section 7).

Consider power consumption in a linear thermochemical system with possible electric fluxes (in case of electrolysers). Assume that a two reservoir arrangement is sufficient to accomplish a separation process or heat pump heating. Both these operations need for their running some instantaneous power supplied to the system. In terms of total resistances of upper and lower parts of two-reservoir system:

$$R\mathrm{s} = R_{1\mathrm{s}} + R_{2\mathrm{s}},\ R_\mathrm{n} = R_{1\mathrm{n}} + R_{2\mathrm{n}},\ R_\mathrm{el} = R_{1\mathrm{e}} + R_{2\mathrm{e}}, \tag{56}$$

and after considering coupled transfer of heat, mass, and electricity, the power supply reads:

$$\begin{aligned} P &= (T_{1'} - T_{2'})I_\mathrm{s} + (\mu_{1'} - \mu_{2'})I_\mathrm{n} + (\phi_{1'} - \phi_{2'})I_\mathrm{e} \\ &= (T_1 - T_2)I_\mathrm{s} + (\mu_1 - \mu_2)I_\mathrm{n} + (\phi_1 - \phi_2)I_\mathrm{e} \\ &+ R_\mathrm{ss}I_s^2 + R_\mathrm{nn}I_n^2 + R_\mathrm{ee}I_e^2 + R_\mathrm{sn}I_sI_n + R_\mathrm{se}I_sI_e + R_\mathrm{ne}I_nI_e \end{aligned} \tag{57}$$

where non-primed quantities refer to bulk states and primed ones to the active, power-consuming part of the system. As shown by this equation, the general thermodynamic framework allows for at least rough assessment of power consumption limits in thermo-electro-chemical systems of the simplest, standardized topology (with no counter-flows). This topology corresponds to a power consumption unit (e.g., heat pump) immersed between two reservoirs, one with high potentials and one with low ones, as described in a number of publications. The reason why this power assessment can only be rough is explicit in Equation (57) which has ignored information about the topological structure of many various flows in the system. Let us also add that possible electrolyzers are also described by the formalism of inert components rather than by the ionic description.

For simplicity, Equation (57) assumes that active (power consuming, primed) driving forces involve only: one temperature difference, trivial chemical affinity and the operating voltage as the difference of the electric potentials. Total power consumption (57) is the sum of thermal, substantial and electric components.

Equation (57) constitutes the simplest account of thermo-electro-chemical separators and heat pumps; indeed it does not contain any "topology parameter". Complex configurations of flows contacting, such as countercurrent contacts, that may exist in fuel cell electrolysers, are not taken into account in Equation (57). Linear systems described by this equation are those with constant (current independent or flux independent) resistances or conductances. They satisfy Ohm type or Onsager type laws linking thermodynamic fluxes and thermodynamic forces (dissipative driving forces which are represented by products $\Sigma R_{ik} I_k$ in Equation (57). While many thermal separation systems and fuel cell electrolyzers are nonlinear, *i.e.*, possess current dependent resistances, the dependence is often weak, so a linear model can be a good approximation. Below, by applying Equation (57) we shall attempt to develop a simple evaluation of power limits for heat pumps and separation systems under the specified assumptions.

After introducing the enlarged flux vector $\mathbf{I} = (I_s, I_n, I_e)$, the enlarged vector of potentials $\tilde{\boldsymbol{\mu}} = (T, \mu, \phi)$, and the related resistance tensor R, Equation (57) can be written in a simple form:

$$P = (\tilde{\boldsymbol{\mu}}_1 - \tilde{\boldsymbol{\mu}}_2).\tilde{\mathbf{I}} - \tilde{\mathbf{R}} : \tilde{\mathbf{I}}\tilde{\mathbf{I}} \tag{58}$$

The bulk driving forces $\boldsymbol{\mu}_1 - \boldsymbol{\mu}_2$ are given constants. Therefore, in systems with constant resistances, we are confronted with a simple minimization problem for a quadratic power consumption function p. While the dimensionality of the potential vector will often be quite large in real systems, the structure of Equation (58) will be preserved whenever the power expression will be considered in the above matrix-vector notation.

Minimum power corresponds with vanishing partial derivatives of function P. The optimal (power-minimizing) vector of currents at the minimum power point of the system can be written in the form:

$$\tilde{\mathbf{I}}_{mp} = -\frac{1}{2}\tilde{\mathbf{R}}^{-1}.(\tilde{\boldsymbol{\mu}}_1 - \tilde{\boldsymbol{\mu}}_2) \equiv -\frac{1}{2}\tilde{\mathbf{I}}_F \tag{59}$$

This result means that the power-minimizing current vector in separators and heat pumps is equal to the negative of one half of the purely dissipative current at the Fourier-Onsager point. The latter point refers to the system's state at which no power production occurs.

Equations (58) and (59) yield the following result for the minimum power input to heat pump or thermal separation system:

$$P_{mp} = -\frac{1}{4}(\tilde{\boldsymbol{\mu}}_1 - \tilde{\boldsymbol{\mu}}_2)\tilde{\mathbf{R}}^{-1}.(\tilde{\boldsymbol{\mu}}_1 - \tilde{\boldsymbol{\mu}}_2) \tag{60}$$

(negative power supply follows because the engine convention is always used, in which power released is positive). In terms of the purely dissipative flux vector at the Fourier-Onsager point, where neither power production nor power consumption occurs, the above limit of minimum power is represented by an equation:

$$P_{mp} = -\frac{1}{4}\tilde{\mathbf{R}} : \tilde{\mathbf{I}}_F \tilde{\mathbf{I}}_{\mathrm{F}} \tag{61}$$

The minus sign corresponds again with the engine convention which requires that power supplied to the system is negative.

On the other hand, the power dissipated at the Fourier-Onsager point is:

$$P_F = \tilde{\mathbf{R}} : \tilde{\mathbf{I}}_F \tilde{\mathbf{I}}_{\mathrm{F}} \tag{62}$$

Comparison of Equations (61) and (62) proves that, in linear thermo-electro-chemical separators with power support, at least 25% of power dissipated in the natural transfer process must be supplied as power surplus in order to run a power-consuming system. Yet, this result may not be exact for systems of complex topology and for those with strong nonlinearities, where significant deviations may be expected.

In fact, the present result describes the largest (most disadvantageous) power surplus that can be approximately applied to real heat pumps, dryers, electrolysers, and other separation systems. For these systems significant deviations from Equations (59)–(61) are nonetheless expected depending on nature of nonlinearities and topology variations, and also on topology improvements to include countercurrent contacting. Despite of the limitation of the result (61) to linear cases, its value is significant because it shows the order of magnitude of thermodynamic limitations in power consumption systems.

The analysis presented here proves that a link exists between the mathematics of heat pumps, separators and electrolysers, and also that, possibly, the theory of electrolysers can be unified with the theory of thermal and chemical separators and heat pumps. All these systems are power consumers. However, serious topological differences between these systems may occasionally render them quite dissimilar.

While the power ratios involving Equations (61) and (62) can be regarded as efficiency measures, they should not be confused with reciprocals of commonly used, popular performance coefficients, especially first law-based coefficients of heat pumps and some separation systems. There are several definitions of performance coefficients, based on first or second laws, proposed for measuring and comparing performance of separation processes. The reciprocals of considered power ratios are the second-law-based performance coefficients which show how closely a concrete process approaches a reversible process.

9. Final Remarks

The example presented in this paper shows how to optimize a drying operation with gas heated by a sequence of heat pumps. The optimization criterion is the power consumption, the optimal solution should assure the minimum of consumed power. The optimal transfer areas are close in value, the optimal temperatures constitute an increasing sequence. The optimal work supplied to the two-stage system decreases distinctly with the total transfer area.

While the present modeling and particular numerical results are limited to multistage operations with heat pumps and continuous co-current dryers with falling particles, after suitable modifications, our approach can be extended to different and more complex configurations.

The practical application of concrete energy sources for drying technology is supported following the theoretical recommendations by introducing the irreversible thermodynamic analysis of the cycles (Mansoori and Patel [32], [Berry *et al.* [33]). Upper and lower limits for the coefficient of performance of solar absorption cooling cycles have been derived from the first and second laws (Mansoori and Patel [32]). 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.

The approach of the "finite time thermodynamics" (FTT) applied in the context of heat pumps has raised an interesting discussion in which its followers and opponents may find lots in common regarding some issues, but also disagree about the others. For example, a renewed and eloquent criticism of the FTT approach was published (Gyftopoulos [34]), corresponding to a number of publications on FTT. Many of the latter papers contain in-depth derivations of the power expression and the Curzon--Ahlborn-Novikov efficiency (CAN efficiency), including thorough explanations of connection between the CAN efficiencies and typical efficiencies of real heat engines (Chen *et al.* [35]) and heat pumps (Li *et al.* [36]). In fact, both types of publications quote some experimental data to support their own conclusions and final stand-point (De Vos [14], Berry *et al.* [33], Chen *et al.* [35]).

The theoretical estimation of minimum work supplied to a heat pump used in the drying technology ought to be compared with the experimental energy consumption criteria. Szwast's exergy optimizations in a class of drying systems with granular solids (Szwast [29], Berry *et al.* [33]) show an agreement of ca 25% between the calculated and experimental consumptions of the propelling exergy. Perhaps the most careful use of the experimental data is given by De Vos who illustrated the practical usefulness of CAN theory for engines exemplified by the quantitative description of the nuclear power plant "Doel 4" in Belgium and explained the difference between the predicted value of engine's optimal efficiency (η_{CAN} = 0.293) and the experimental thermal efficiency (η_{exp} = 0.350). By simple economical considerations De Vos also explained why the actual efficiency of the engine is larger than its CAN efficiency (De Vos [14]).

This research provides data for power production limits which are enhanced in comparison with those predicted by the classical thermodynamics. In fact, thermo-static limits are often too distant from reality to be really useful. Generalized limits, obtained here, are stronger than those predicted by the thermostatic theory. As opposed to classical thermodynamics, generalized limits depend not only on state changes of resources but also on process resistances, process direction and mechanism of heat and mass transfer. A common methodology has been developed for thermal, chemical and electrochemical systems. As shown in our earlier papers, fuel cells are included into this methodology (Li [37]).

The main methodological novelty of the paper lies in the synthesizing nature of its approach, which includes fuel cells in the common class of thermodynamic power yield systems. In the thermodynamic optimization, considered here, *i.e.*, the optimization applying thermodynamic constraints and performance criteria, thermodynamic synthesis expresses an idea of combining various partial optimization models into a “synthesizing” (not necessarily “generalizing”) model from which performances of all the component units can be predicted. We have shown that, with irreversible thermodynamics, we can predict the performance behaviour and power limits for quite diverse practical systems.

In comparison with the previous publications, canonical (Hamiltonian) treatment of optimal dynamical processes constitutes a novel approach which should be contrasted with the dynamic programming approaches (DP approaches) developed in the earlier publications [1–3,13]. Since the analytical treatment of differential optimization models (such as those in Equations (9) and (10) of the present paper) is most often a very difficult task, solving techniques used previously treated numerically Bellman's recurrence equation of a dynamic programming model (DP model). However, DP approaches are effective only for low dimensionality of the state vector. As the number of state variables in chemical systems is usually large (many concentrations may accompany temperature and catalyst activities), DP algorithms become inefficient and inaccurate in real systems.

Therefore, in this paper, we have limited the DP approaches to special cases of low state dimensionality and developed the Pontryagin type (Hamiltonian-based) approaches, Section 5. The novel technical core of the present work is the development and application of Pontryagin's type (Hamiltonian-based) approaches to optimal power systems. As opposed to the dynamic programming algorithms (DP algorithms, applied earlier), Hamiltonian algorithms, which involve discrete or difference equations rather than DP recurrence equations, are particularly effective in power systems with large dimensionality of the state vector. There is also a novelty in the mathematical structure of Hamiltonians applied here, which admit discrete process rates as entities explicitly dependent on time intervals, θ. Until now Hamiltonians were used in power systems quite seldom, and were limited to models with θ- independent discrete rates, the models which sometimes prove to be oversimplified [10,38,39].

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Appendix: Entropy Source and Power Yield in Terms of Carnot Variables

Consider entropy generation in a diffusion limited power system *i.e.*, the system in which contributions following from the role of convective (bulk) motion are negligible. Balance of fluxes involving intensive thermal parameters in the bulks of the streams yields:

$$\sigma_s = \frac{q_2}{T_2} - \frac{q_1}{T_1} + (s_2 - s_1)n_1 \tag{A1}$$

This expression contains classical heat fluxes q_1 and q_2 identified with the so-called senstive heat (the heat attributed to thermal agitations in the continuum medium). In this paper we shall also define and use other flux related to heat q, the so-called total heat flux which contains the product of temperature T and the sum of partial entropies of the species multiplied by the involved mass fluxes:

$$Q = q + T(s_a n_a + s_b n_b .... + s_k n_k) \tag{A2}$$

We shall also use total energy flux, ε, defined in accordance with the usual definition, that is as the quantity:

$$\varepsilon = q + h_a n_a + h_b n_b .... + h_k n_k \tag{A3}$$

Note that, as a consequence of the definition of Q, the internal entropy balance of a perfect engine driven by both heat and mass transfer has, in terms of total heat flux Q, the same structure as in purely thermal systems:

$$\frac{Q_2}{T_{2'}} = \frac{Q_1}{T_{1'}} \tag{A4}$$

Eliminating heat flux q_2 from Equation (A1) with the help of the engine's energy balance:

$$\varepsilon_1 = \varepsilon_2 + p \tag{A5}$$

and applying the mass balance of a reacting system with a complete conversion in terms of conserved fluxes through cross-sections 1-1' and 2'-2:

$$n_1 = n_2 \tag{A6}$$

(compare primed generator states with non-primed bulk states in Figures 1 and 2) we obtain:

$$\sigma_s = (q_1 + h_1 n_1)(\frac{1}{T_2} - \frac{1}{T_1}) + (\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2})n_1 - \frac{p}{T_2}. \tag{A7}$$

where the sum $q_1 + h_1 n_1$ is the total energy flux ε_1 in the system with a complete conversion. A transformed form of this equation is the power formula:

$$p = \varepsilon_1 (1 - \frac{T_2}{T_1}) + T_2 (\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}) n_1 - T_2 \sigma_s \tag{A8}$$

which links power output p with bulk parameters of reservoirs and entropy production σ_s in the system.

Equation (A10) may be compared with the same power evaluated for the endoreversible part of the system. Combining the mass balance (A6) with an equation describing the continuity of the rev ersible entropy flux:

$$\frac{\varepsilon_1 - \mu_{1'} n_1}{T_{1'}} = \frac{\varepsilon_2 - \mu_{2'} n_2}{T_{2'}} \tag{A9}$$

and eliminating from this result ε_2 and n_2 with the help of Equations (A5) and (A6) yields:

$$\frac{\varepsilon_1 - \mu_{1'} n_1}{T_{1'}} = \frac{\varepsilon_1 - p - \mu_{2'} n_1}{T_{2'}} \tag{A10}$$

which leads to the power expression:

$$p = \varepsilon_1 (1 - \frac{T_{2'}}{T_{1'}}) + T_{2'} (\frac{\mu_{1'}}{T_{1'}} - \frac{\mu_{2'}}{T_{2'}}) n_1 \tag{A11}$$

Power p is expressed in terms of fluxes continuous through the conductors. Equation (A11) may be regarded as a consequence of Equation (A8) when it is applied to the reversible zone of the system.

After comparing Equations (A8) and (A11) we obtain an equality:

$$\begin{aligned}&\varepsilon_1(1-\frac{T_2}{T_1})+T_2(\frac{\mu_1}{T_1}-\frac{\mu_2}{T_2})n_1-T_2\sigma_s\\&=\varepsilon_1(1-\frac{T_{2'}}{T_{1'}})+T_{2'}(\frac{\mu_{1'}}{T_{1'}}-\frac{\mu_{2'}}{T_{2'}})n_1\end{aligned} \tag{A12}$$

from which entropy production can be expressed in terms of bulk driving forces and active driving forces (measures of process efficiencies). Finally we arrive at the result:

$$\begin{aligned}\sigma_s &= \frac{\varepsilon_1}{T_2}(\frac{T_{2'}}{T_{1'}}-\frac{T_2}{T_1})\\&+n_1(\frac{\mu_1}{T_1}-\frac{T_{2'}}{T_2}(\frac{\mu_{1'}}{T_{1'}}-\frac{\mu_{2'}}{T_{2'}})-\frac{\mu_2}{T_2}).\end{aligned} \tag{A13}$$

which expresses entropy production in terms of bulk properties of streams and (primed) properties of the power producing zone in the system.

Introducing an effective temperature called Carnot temperature:

$$T' \equiv T_2 T_{1'}(T_{2'})^{-1} \tag{A14}$$

we note that the endoreversible thermal efficiency in Equation (A11) satisfies the Carnot formula in terms of T' and T_2:

$$\eta = 1-\frac{T_{2'}}{T_{1'}} = 1-\frac{T_2}{T'} \tag{A15}$$

The name *Carnot temperature* is used for the quantity T' simply because the efficiency of an internally reversible engine expressed in terms of T' and T_2 satisfies the Carnot formula. When an input energy flux is given, Equation (A15) is suitable to determine power production or consumption in various steady and unsteady systems. Whenever internal dissipation effects prevail in the power generation zone, an effective environment temperature ΦT_2 should appear in Equation (A15) in place of T_2 (Section 2).

In dynamical thermal systems a state trajectory is a curve $T_1 = T(t)$ which describes the change of temperature of the resource fluid in time, whereas a control curve may be represented by efficiency $\eta(t)$ or Carnot temperature $T'(t)$. The latter quantity, defined by Equation (A14), is particularly suitable in describing driving forces and resource relaxations in dynamical energy systems. Whenever $T'(t)$ differs from $T(t)$ the resource is relaxing to the environment with a finite rate associated with the efficiency deviation from the Carnot efficiency. Only when $T'(t) = T(t)$ the efficiency is Carnot, but this corresponds with an infinitely slow relaxation rate of the resource to the thermodynamic equilibrium. In real processes (those with finite relaxation rates) thermal efficiencies are always lower than Carnot, corresponding with Carnot temperatures $T'(t)$ lower than the resource temperatures $T(t)$. In chemical systems the role similar to T' is played by the Carnot chemical potential, described below.

Also, in terms of Carnot T', an endoreversible part of the entropy production (A13) for a pure heat process, takes the following simple form:

$$\sigma_s = q_1(\frac{1}{T'}-\frac{1}{T_1}) \tag{A16}$$

Consequently, Equation (A13) generalizes the familar entropy production expression (A16) for the case when a single reaction $A_1 - A_2 = 0$, undergoes in the system [1,13].

Equation (A13) also leads to the definition of Carnot temperature (A14) and to Carnot chemical potential of the first component:

$$\frac{\mu'}{T'} = \frac{\mu_2}{T_2} + \frac{T_{2'}}{T_2}\left(\frac{\mu_{1'}}{T_{1'}} - \frac{\mu_{2'}}{T_{2'}}\right) \tag{A17}$$

In the special case of an isothermal process the above formula yields a chemical control:

$$\mu' = \mu_2 + \mu_{1'} - \mu_{2'} \tag{A18}$$

which has been used earlier to study an isothermal chemical engine [3].

After introducing the Carnot potentials in accordance with Equations (A14) and (A17), total entropy production of the endoreversible power generation by the simple reaction $A_1 - A_2 = 0$ (isomerisation or phase change of A_1 into A_2), takes the following simple form:

$$\sigma_s = \varepsilon_1\left(\frac{1}{T'} - \frac{1}{T_1}\right) + \left(\frac{\mu_1}{T_1} - \frac{\mu'}{T'}\right)n_1 \tag{A19}$$

Introducing into the above formula total heat flux Q_1, satisfying in the considered case an expression $Q_1 \equiv \varepsilon_1 - \mu_1 n_1$, we finally obtain:

$$\sigma_s = Q_1\left(\frac{1}{T'} - \frac{1}{T_1}\right) + n_1 \frac{\mu_1 - \mu'}{T'} \tag{A20}$$

where the total heat flux Q_1 can also be expressed as the sum $Q_1 = q_1 + T_1 s_1 n_1$. The resulting Equations (A19) and (A20) are formally equivalent to an expression obtained for the process of purely dissipative exchange of energy and matter between two bodies with temperatures T_1 and T' and chemical potentials μ_1 and μ'.

Examples considered in the main text of the present paper refer first to classical and radiation thermal machines and next to chemical and electrochemical power generators (fuel cells). Ideas referring to endoreversible systems are generalized to those with internal dissipation.

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