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Analysis of power and entropy generation in a chemical engine

Stanislaw Sieniutycz

Faculty of Chemical Engineering, Warsaw University of Technology, 1 Warynskiego Street, 00-645 Warsaw, Poland

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ABSTRACT

We develop a thermodynamic theory for a difficult class of chemical processes undergoing in irreversible power-producing systems that yield mechanical work and are characterized by multiple (vectorial) efficiencies. Obtained efficiency formulas are applied for chemical machines working at maximum production of power. Steady-state model describes a chemical system in which two reservoirs are infinite, whereas an unsteady model treats a dynamical system with finite upper reservoir and gradually decreasing chemical potential of a key fuel component. In the considered chemical systems total power output is maximized at constraints which take into account dynamics of mass transport and efficiency of power generation. Dynamic optimization methods, in particular variational calculus, lead to optimal functions that describe integral power limits and extend reversible chemical work W_{rev} to finite rate situations. Optimization results quantify effects of chemical rates and transport phenomena. Legendre transform of a local power function is an effective tool to obtain an optimal path in a dynamical process of power yield.

1. Introduction

In this work, we analyze the performance of a non-isothermal chemical engine in terms of heat and mass fluxes flowing from a fuel reservoir to the power generator. By assumption, a fuel mixture that drives the power generator is composed of an inert and an active component. Efficiency, power yield, and fuel flux are essential variables determining the performance of the chemical system [1–3]. The problem of finite-rate limits, which was treated in our earlier papers for thermal processes [4–6], is applied here to chemical systems, steady and unsteady. Enhanced limits caused by finite rates are evaluated for power released from an engine system or added to a power consuming system.

We discuss two basic models of chemical units producing power. Steady-state model, originated in [1,2], refers to the situation when both reservoirs are infinite, whereas a new, unsteady model treats a dynamical case with finite upper reservoir and gradually decreasing chemical potential of the active component of fuel. As opposed to the earlier works [1,2], we extend the original problem to situations with non-isothermal generation of power. In the dynamical case Lagrangian and Hamiltonian approaches to power functionals and optimization algorithms using canonical equations are effective. Finite-rate models incorporate a minimum entropy production caused by irreversible diffusion phenomena.

Modeling a power-assisted chemical operation for the purpose of dynamic limits is a difficult task. Evaluation of dynamic limits requires sequential operations [3–6], where total power yield is maximized at constraints which describe dynamics of energy and mass exchange. The dynamical model can be continuous or discrete; the latter are frequent for computational purposes. The results are limiting work functions in terms of end states, duration and (in discrete processes) number of stages [5]. Modeling of power generation processes is consistent with general philosophy of optimization [7–9]. Constraints take into account dynamics of mass transport and rates of fuel consumption. Finite-rate, endoreversible modeling includes irreducible losses of classical exergy caused by resistances. Optimal performance functions, which describe extremum power and incorporate a residual minimum entropy production, are determined in terms of end states, duration and (in discrete processes) number of stages [5,10]. Similarly as in thermal systems enhanced power limits follow from the constrained optimization of total power.

In chemical engines mass transport processes participate in the transformation of differences of chemical potentials into mechanical power. However, a more precise statement refers not to the individual chemical potentials μ_k, but to their linear combination in the form of uni-directional component of chemical affinity, Π_j [11]. This affinity component is, in fact the potential Π_j of the reagents that decreases along the reaction path. The quantity Π_j (which reduces to the chemical potential of a single component only in the case of a simplest isomerisation reaction) plays in chemical engines role analogous to that played by the temperature in heat engines. Yet, in chemical systems, generalized reservoirs are present that are capable of providing heat and substance. Heat conductors of the thermal engine theory became conductors of both matter and substance in the chemical engine theory.

E-mail address: sieniutycz@ichip.pw.edu.pl

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Nomenclature

A, A^{class}	molar generalized and classical exergy (J mol^{-1})
A	chemical affinity of reaction (J mol^{-1})
$A_{\text{C}} = -\Delta G$	chemical affinity at Carnot point (J mol^{-1})
A^k	total exchange area at stage k (m^2)
a_v	specific area per unit volume (m^{-1})
c_p	molar heat capacity at the constant pressure ($\text{J mol}^{-1}\text{K}^{-1}$)
c_m	mass capacity of the active component of fuel ($\text{mol}^2\ \text{J}^{-1}$)
F	area of surface perpendicular the flux direction (m^2)
f_0, f_i	process rates
G	Gibbs energy flux driving chemical engine (J s^{-1})
g_1, g	partial and overall conductance (mol s^{-1})
H	Hamiltonian
h_σ	Hamiltonian density in entropy units ($\text{J m}^{-3}\ \text{K}^{-1}$)
H_{TU}	height of mass transfer unit (m)
I	molar flux of inert component (mol s^{-1})
k	stage number
l	transfer area coordinate, variable of spatial extent of the system (m)
N^k	cumulative flux of mole number for stages $1,2,\ldots,k$ (mol s^{-1})
n	diffusive flux of mole numbers, invariant flux of active components of the fuel mixture (mol s^{-1})
P, p	cumulative power output and power output (J s^{-1})
Q	heat flux including effect of mass transfer (J s^{-1})
q	sensible heat flux (J s^{-1})
R	gas constant ($\text{J K}^{-1}\ \text{mol}^{-1}$)
$R(X,t)$	optimal work function of cost type in terms of state and time (J mol^{-1})
r	chemical reaction rate ($\text{mol m}^{-3}\ \text{s}^{-1}$)
S	entropy (J K^{-1})
S_σ	molar entropy production ($\text{J K}^{-1}\ \text{mol}^{-1}$)
T	temperature of controlled phase (K)
T_1, T_2	bulk temperatures of reservoirs 1 and 2 (K)
$T_{1'},\ T_{2'}$	temperatures of fluid circulating in thermal engine (K)
T^{e}	constant equilibrium temperature of environment (K)
T'	Carnot temperature (K)
$\dot{T} = u$	rate of temperature change in non-dimensional time (K)
t	physical time, contact time (s)
$\mathbf{u}$	control vector
u	variable controlling the fuel consumption
$V = \max(W)$	optimal work function of profit type (J mol^{-1})
v	velocity (m s^{-1})
$W = P/G$	total specific work or total power per unit molar flux
W	molar work at flow, total power per unit mass flux of inert (J mol^{-1})
X	concentration of active component in fuel, moles per mole of inert (mol mol^{-1})
$\dot{X} = \text{d}X/\text{d}\tau_1$	rate change of fuel concentration in time τ_1
x	molar fraction of active component in the fuel (mol mol^{-1})
$x_{1'}$	molar fraction of reactant in chemically active part of the system (mol mol^{-1})
$x_{2'}$	molar fraction of product in chemically active part of the system (mol mol^{-1})
z	adjoint variable

Greek symbols

α'	overall heat transfer coefficient ($\text{J m}^{-2}\ \text{s}^{-1}\ \text{K}^{-1}$)
β'	overall mass transfer coefficient ($\text{mol m}^{-2}\ \text{s}^{-1}$)
γ	cumulative conductance of the system ($\text{J s}^{-1}\ \text{K}^{-1}$)
ε	pseudoenergy as the Legendre transform of a Lagrangian
$\zeta = \mu_{1'} - \mu_{2'}$	efficiency of chemical engine as active part of chemical affinity (J mol^{-1})
ζ_{mp}	efficiency of chemical engine at maximum power point (J mol^{-1})
$\eta = p/q_1$	first-law thermal efficiency
θ	time interval referred to non-dimensional time τ_1, Eq. (77), and conductance g_1
λ	Lagrange multiplier (J mol^{-1})
μ	chemical potential (J mol^{-1})
μ'	Carnot chemical potential for active component of fuel (J mol^{-1})
μ_1	chemical potential of active component of fuel (J mol^{-1})
ξ	process intensity factor
Π_j	one-directional part of chemical affinity for jth reaction (J mol^{-1})
σ_{s}	intensity of entropy production ($\text{J K}^{-1}\ \text{m}^{-3}\ \text{s}^{-1}$)
τ	non-dimensional time, number of transfer units (x/H_{TU})
Φ	factor of internal irreversibility
χ	state vector

Subscripts

C	Carnot state (open circuit)
i	state variable index
j	reaction number
v	per unit volume
1, 2	components 1 and 2

Superscripts

e	environment
i	initial state
f	final state
$'$	Carnot quantity
0	reference state

Infinite reservoirs are capable of keeping constant the process potentials $(T, \mu_k, \Pi_j, \ldots)$. For such reservoirs problems of extremum power (maximum of power produced and minimum of power consumed) are static optimization problems. On the other hand, for finite reservoirs, in which the amount of an active reactant is gradually reduced and its chemical potential decreases in time, the considered problems are those of dynamic optimization.

To deal with steady situations, we consider a single 'endoreversible' chemical machine, an engine or power consumer, in Fig. 1. The engine is propelled by a high-μ active reactant of a fluid mixture (fuel mixture) that is supplied to the power generator from an infinitely large reservoir. The fluid mixture is composed of the active reactant and an inert. The flux of active reactants designated by n, influences the intensity of power yield, where $n = n_{1'}$ for the substrate and $n = n_{2'}$ for the product.

Yet, tackling a dynamical situation requires considering a multistage production (consumption) of power in a sequence of chemical engines. This case is associated with a finite upper reservoir and a gradual exhaust of the active reactant in the fuel mixture. In the multistage engine the chemically active reactant drives at each stage the chemical power generator from which power is released. In the multistage power consumer the fuel mixture is upgraded in the system to which power is supplied. In each case the second fluid is an infinite reservoir. The fluids are of finite thermal and mass conductivity, hence there are finite resistances in the system. In a multistage engine operation the driving chemical potential decreases at each stage; the whole operation is described by the sequence $\mu^0, \mu^1, \ldots, \mu^N$. The popular 'engine convention' is used: work generated in an engine, W, is positive, and work generated in a power consumer is negative; this implies a positive work $(-W)$

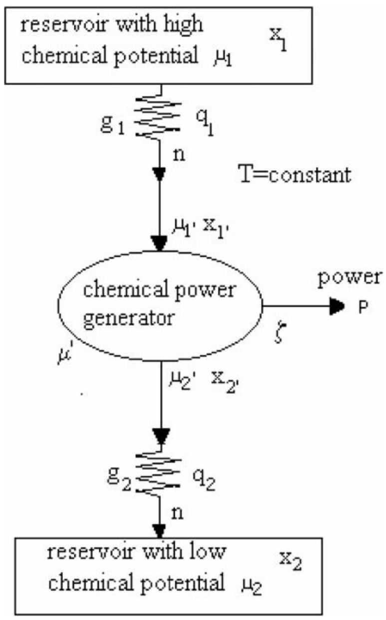

Fig. 1. Principle of a chemical engine driven by transfer of an active component through an inert.

consumed in the power consumer. The sign of an optimal work function $V^N = \max W^N$ defines working mode for an optimal sequential process as a whole. In engine modes $W > 0$ and $V > 0$. In power consumption 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 $X^0 = X^e$ and terminates at an arbitrary $X^N = X$ and the one which starts at an arbitrary $X^0 = X$ and terminates at X^e. For these processes functions V^N and R^N are counterparts of the classical exergy in state changes with finite durations.

The topological nature of the state space and its influence on the system dynamics are determined by both the state of the finite-resource fuel flowing through stages of the cascade and the properties of the heat bath (infinite thermal reservoir). Without bath the dynamic topology would correspond to a simple sequence of stages (a cascade) with the state dimensionality defined by the number of independent coordinates of the fuel mixture. The presence of an infinite bath, the intensive parameters of which, i.e. its temperature T^e and chemical potentials μ_i^e, do not change along the process path, introduces into the mathematical model constant parameters T^e and μ_i^e. In fact, it is the condition of an infinite bath that enables us to treat all power functions p^n as the bath-history independent. The potential function of extremum work, obtained via optimization of a work integral, is of exergy type, i.e. it contains intensive parameters of the bath and state coordinates of the fuel mixture. This property makes the (parameter dependent) function of extremum work different from the (parameter independent) thermodynamic potentials.

The range of optimization in this paper is restricted to thermodynamic limits, or, more specifically, to a generalized quantity of exergy type attributed to the single stream of fuel. This quantity constitutes a generalized potential of extremum work that depends on end states of the fuel mixture and its holdup time in the system (time of fuel consumption). Alternatively, a generalized potential could be expressed in terms of end states of the fuel stream and the optimal Hamiltonian that is a measure of the process intensity along an optimal path.

Generalized (dissipation-affected) power limits for a finite time degrading of the fuel mixture are the main task of this paper. To find these limits the system unit must contain a chemically active part or a "reaction zone". Only in "endoreversible" systems this zone is a purely reversible part of the system, i.e. its efficiency of energy production is given by a reversible formula. This reversible formula constitutes a chemical counterpart of the familiar Carnot formula $\eta_C = 1 - T_2/T_1$, valid for thermal engines. In chemical engines, however, the reversible formula refers to the chemical affinity, which has nothing in common with the Carnot efficiency, η_C.

Yet, the restriction to external irreversibilities is unnecessary; in fact, thermodynamic models can go beyond "endoreversible limits" i.e. they can treat internal irreversibilities as well, see Refs. [5,6,12,13]. It is most essential, however, that in either of two methodological versions of the thermodynamic approach, of which the first gives up internal irreversibilities whereas the second one estimates these from a model, the obtained power limits are stronger than those predicted by the classical exergy. In short, this results from the "process rate penalty" that is taken into account in every version of the approach.

In classical Carnot-like analyses the resource and environment reservoirs are insensitive to the effect of dissipators (boundary layers, resistances, etc.) because the reversible situation requires the spatial homogeneity of each reservoir. In the irreversible analysis, performed here, which admits dissipative transports, inhomogeneities in transport potentials play essential role.

When calculating power limits, we search for *purely physical* extrema with no regard to economic optima.

2. Thermodynamics of power generation in non-isothermal chemical engines

This section analyzes a single-stage chemical process depicted in Fig. 1. To obtain a power yield formula associated with a single isomerisation reaction

$$B_1 \Longleftrightarrow B_2$$

we apply balances of energy, entropy and mass. We assume that an active reagent 1 and the sensible heat q_1 are transferred to the reaction zone through an inert gas. As the result of the chemical transformation the reaction zone yields product 2 which is transferred through the same inert gas to the environment. The energy balance

$$\varepsilon_1 = \varepsilon_2 + p \tag{1}$$

and the mass balance in terms of molar fluxes

$$n_1 = n_{1'} = n_{2'} = n_2 \tag{2}$$

are combined with an equation describing the continuity of the entropy flux

$$\frac{\varepsilon_1 - \mu_{1'} n_{1'}}{T_{1'}} = \frac{\varepsilon_2 - \mu_{2'} n_{2'}}{T_{2'}} \tag{3}$$

Eq. (3) holds in the chemically active, reversible part of the system where the chemical reaction runs.

Eqs. (1)–(3) yield the power expression

$$p = \varepsilon_1 - \varepsilon_2 = \left(1 - \frac{T_{2'}}{T_{1'}}\right)\varepsilon_{1'} + T_{2'}\left(\frac{\mu_{1'}}{T_{1'}} - \frac{\mu_{2'}}{T_{2'}}\right) n_{1'} \tag{4}$$

The energy flux in the dissipative parts of the system is continuous, for example

$$\varepsilon_1 = q_1 + h_1 n_1 = q_{1'} + h_{1'} n_{1'} = \varepsilon_{1'} \tag{5}$$

Using the primed part of this equation in the power formula (4) yields

$$p = \left(1 - \frac{T_{2'}}{T_{1'}}\right) q_{1'} + [(h_{1'} - h_{2'}) - T_{2'}(s_{1'} - s_{2'})] n_{1'} \tag{6}$$

Thus, the combination of the second law and the reversible balance of the entropy leads to power expression (6) in which the Carnot efficiency of an endoreversible process

$$\eta = 1 - \frac{T_{2'}}{T_{1'}} \tag{7}$$

is the thermal component of a two-dimensional efficiency vector. The second component of this vector is the exergy-like function of the active component evaluated for the primed state 2 as the reference state

$$\beta' = h_{1'} - h_{2'} - T_{2'}(s_{1'} - s_{2'}) \tag{8}$$

Observe that in the considered case (where molar flux n is the efficiency basis) the chemical component of efficiency is not non-dimensional. Other cases of this sort will be observed later when we shall also note the identity of efficiencies with active driving forces. The primed quantities and equations are often applied in a transformed form expressing all physical quantities in terms of the bulk state variables of both fluids and certain controls. The latter are related to fluxes of heat and matter. Applying the energy flux continuity and mass flux continuity in Eq. (6) to eliminate fluxes $q_{1'}$ and $n_{1'}$ on account of q_1 and n_1 yields

$$p = \left(1 - \frac{T_{2'}}{T_{1'}}\right) q_1 + \beta n_1 \tag{9}$$

where coefficient β is defined as

$$\beta = \left[c_p(T_1 - T_{1'})\left(1 - \frac{T_{2'}}{T_{1'}}\right) + (h_{1'} - h_{2'}) - T_{2'}(s_{1'} - s_{2'})\right] n_1 \tag{10}$$

Note bilinear power structures in Eqs. (6) and (9), cf. [5]. Both these equations are useful measures of chemical efficiency, yet they differ in the heat flux (q_1 or $q_{1'}$) accepted as the control variable. The second component of power expressions (6) and (9) is associated with the work production (consumption) due to the mass transfer. Its interpretation is the product of mass flow n and exergy-like functions β' or β whose structure follows from combination of the energy and (conservative) entropy balances.

Yet, we may eliminate exergy-like functions β and β' by passing to the process description in terms of different fluxes. Leaving mass flux n unchanged, we introduce a new energy flux, $Q_{1'}$, called total heat flux, which is defined by an equation

$$Q_{1'} \equiv q_{1'} + T_{1'} s_{1'} n_{1'} \tag{11}$$

Clearly, $Q_{1'}$ is the product of temperature $T_{1'}$ and the total entropy flux, the latter being the sum of entropy transferred with heat $q_{1'}/T_{1'}$ and with substance $s_1 n_1$. The virtue of flux $Q_{1'}$ is that the power production $p = \dot{w}$ assumes in terms of $Q_{1'}$ a most suitable form that contains the product of the chemical potential difference of the active components and the invariant flux n

$$\dot{w} = p = \left(1 - \frac{T_{2'}}{T_{1'}}\right) Q_{1'} + (\mu_{1'} - \mu_{2'}) n \tag{12}$$

In this case the chemical efficiency component is just the chemical affinity for the single isomerisation reaction considered.

Alternatively, we may base the efficiency on a certain mass analogue of heat flux $Q_{1'}$ defined as follows

$$G_{1'} \equiv \mu_{1'} n_{1'} \tag{13}$$

The quantity $G_{1'}$ is, in fact, the flux of Gibbs free energy of the active component of fuel. The suitability of this quantity, which we call Gibbs flux, follows from its capability of measuring quality of mass flux $n_{1'}$. In fact, flux $G_{1'}$ measures the quality of $n_{1'}$ in the same way as heat $Q_{1'}$ measures the quality of entropy flux; the associated "quality potentials" being respectively $\mu_{1'}$ and $T_{1'}$. With Eq. (13) power expression (12) is

$$p = \left(1 - \frac{T_{2'}}{T_{1'}}\right) Q_{1'} + \left(1 - \frac{\mu_{2'}}{\mu_{1'}}\right) G_{1'} \tag{14}$$

The entropy and mass balances of an endoreversible machine take in terms of variables $Q_{1'}$ and $G_{1'}$ the following simple forms

$$Q_{1'}/T_{1'} = Q_{2'}/T_{2'} \tag{15}$$

$$G_{1'}/\mu_{1'} = G_{2'}/\mu_{2'} \tag{16}$$

When the Gibbs flux is the efficiency basis the structure of the mass transfer balance (16) is formally the same as that of the heat transfer balance (15). Note that the endoreversible thermal efficiency in terms of properties of the circulating fluid is the same as in the process of pure heat transfer, i.e. it has the Carnot form.

The power expression in "the flux representation" conforms with the general structure

$$p = \dot{w} = \eta(Q_{1'}, G_{1'}) Q_{1'} + \omega(Q_{1'}, G_{1'}) G_{1'} \tag{17}$$

Total heat flux $Q_{1'}$ and Gibbs energy flux $G_{1'}$ are two independent fluxes driving the process of power production.

In a traditional analysis power (14) may be considered in terms of two unknown ("primed") temperatures and two unknown ("primed") chemical potentials of circulating fluid, these variables being linked by entropy and mass balances across the reversible part of the system. Such balance constraints make equations quite difficult to use, and a method to overcome the difficulty should be designed. The so-called Carnot quantities [1,4,14], play in this matter an essential role.

3. Non-isothermal engines in terms of Carnot variables

We shall now pass to corresponding relationships in terms of the Carnot variables [1,4]. The rationale for their use follows from the fact that temperatures and chemical potentials of circulating fluid are not independent variables but they are constrained by balances of entropy and substance through the engine. Application of Carnot variables leads to the process description (consistent with the entropy and mass balances) in terms of free controls that assure suitable formulae for efficiency, heat and mass fluxes, and power. Carnot temperature was comprehensively discussed earlier [4,14]. The present text gives the good opportunity to discuss various definitions of the Carnot chemical potential, and the choice of the most suitable one.

An easiest formal way to set a suitable definition of a Carnot variable is to assume the invariance of efficiency, η or ω. Considering, for example $1 - \omega$, we obtain the equality

$$\frac{\mu_{2'}}{\mu_{1'}} = \frac{\mu_2}{\mu'} \tag{18}$$

(possible coefficients of internal irreversibilities cancel in these expressions). Definition of the Carnot chemical potential then follows as

$$\mu' \equiv \frac{\mu_{1'}}{\mu_{2'}} \mu_2 \tag{19}$$

Thus, when the chemical efficiency is based on the Gibbs energy flux (and only in this case) the expression describing the Carnot chemical potential is fully analogous to that describing the Carnot temperature

$$T' \equiv \frac{T_{1'}}{T_{2'}} T_2 \tag{20}$$

For the latter quantity, see Refs. [4,14]. The definition of Carnot temperature T' remains unchanged when the mass transfer accompanies the heat transfer.

The thermal efficiency is the first component of two-dimensional efficiency vector. For the thermal efficiency in terms of Carnot temperature, we find

$$\eta = 1 - \frac{T_2}{T'} \tag{21}$$

The second efficiency component is related to the difference of chemical potentials

$$\omega = 1 - \frac{\mu_2}{\mu'} \tag{22}$$

As the Gibbs flux is the efficiency basis and Eqs. (13), (14), (16) and (17) hold, the chemical efficiency (22) has the Carnot form.

However, in terms of variables $Q_{1'}$ and $n_{1'}$ the chemical efficiency is neither non-dimensional nor of the Carnot structure; rather it follows in the affinity units

$$\zeta \equiv p/n \equiv \mu_{1'} - \mu_{2'} \tag{23}$$

whereas the associated Carnot chemical potential of the active component is [1]

$$\mu' \equiv \mu_2 + \mu_{1'} - \mu_{2'} \tag{24}$$

Of course, the chemical efficiency (23) has dimensional units, those of energy per mole. As Eq. (20), Eq. (24) is the trivial consequence of the efficiency invariance, $\mu_{1'} - \mu_{2'} = \mu' - \mu_2$. In the reversible case, i.e. when $\mu_{1'} = \mu_1$ and $\mu_{2'} = \mu_2$, expression (24) reduces μ' to μ_1, thus, in this case, the chemical component of the efficiency vector equals $\mu_1 - \mu_2$. Note the direct link between efficiencies and driving forces. For example, efficiency (23) is the driving force describing the chemical affinity of the isomerisation reaction considered.

Carnot chemical potential, μ', should be redefined when a more usual energy flux $\varepsilon = q + \sum h_i n_i$ is applied instead of Q. In this case Eq. (4) leads to the following definition of Carnot chemical potential μ' in terms of parameters of circulating fluid (T'_1, T'_2, $\mu_{1'}$ and $\mu_{2'}$)

$$\mu' = T'(\mu_2/T_2 + (T_{2'}/T_2)(\mu_{1'}/T_{1'} - \mu_{2'}/T_{2'})) \tag{25}$$

This quantity, which was occasionally used in some of our previous papers (see, e.g. [4,14]) is equivalent with μ' of Eq. (24) only in an isothermal case. Chemical potentials in Eqs. (19), (22) and (23) are all correct still they differ because each refers to a different pair of fluxes. In any process with mass transfer the work yield is characterized by the vector of thermal efficiencies (η,ω), such that its first component is the Carnot efficiency.

Thermodynamic functions of state referred to Carnot temperatures and chemical potentials are called Carnot functions. One may always pass to corresponding relationships in terms of "thermodynamic Carnot quantities". In this way one may deal with Carnot energy, enthalpy, entropy, etc. Importantly, in terms of Carnot thermodynamic variables, reversible structure of basic equations is preserved in irreversible cases, and prediction is possible of irreversible equations on the basis of well-known or easily derived equations of reversible processes.

At the "short circuit point" [2] the equalities $T' = T_2$ and $\mu' = \mu_2$ hold and all components of efficiency vector (η,ω) do vanish. Yet, at the "Carnot point" [2] efficiencies refer to the quasistatic process. In this (reversible) case efficiency vector in Eq. (14) has the components

$$\eta_C = 1 - \frac{T_2}{T_1} \tag{26}$$

and

$$\omega_C = 1 - \frac{\mu_2}{\mu_1} \tag{27}$$

Leaving aside other special cases and returning to the problem in terms of $Q_{1'}$ and $G_{1'}$ we can state that a general optimization task is to seek for optimal T' and μ' which maximize power p in "Carnot variables representation"

$$\begin{aligned}
p &\equiv \dot{w} \\
&= \eta(T', T_2)Q_{1'}(T', T_1, \mu', \mu_1) + \omega(\mu', \mu_2)G_{1'}(T', T_1, \mu', \mu_1) \\
&= (1 - T_2/T')Q_{1'} + (1 - \mu_2/\mu')G_{1'} \\
&= (1 - T_2/T_1)Q_{1'} + (1 - \mu_2/\mu_1)G_{1'} - T_2 Q_{1'}(1/T' - 1/T_1) \\
&\quad + \mu_2 G_{1'}(1/\mu_1 - 1/\mu')
\end{aligned} \tag{28}$$

The expression in the second line is the irreversible power expression that was split into the reversible part (two expressions in the third line without Carnot controls) and an irreversible part (the expression which is the negative product of T_2 and entropy production). Note that Carnot temperature and Carnot chemical potential are independent variables and the power is extremized with respect to these variables as free process controls. The reversible balances of entropy and mass across the (perfect) thermal machine are included; thus the extremizing procedure works without constraints.

4. Entropy production in steady systems

Let us determine an expression for the entropy production from the entropy balance of a steady system. From the entropy balance of an overall system composed of reservoirs and reactor the intensity of the entropy production σ_s follows in terms of the reservoir parameters and system fluxes

$$\sigma_s = \frac{q_2}{T_2} - \frac{q_1}{T_1} + (s_2 - s_1)n \tag{29}$$

Using in this equation the energy conservation law

$$q_1 + h_1 n = q_2 + h_2 n + p \tag{30}$$

to eliminate flux q_2, we obtain

$$\sigma_s = \frac{q_1 + h_1 n - h_2 n - p}{T_2} - \frac{q_1}{T_1} + (s_2 - s_1)n \tag{31}$$

Whence, in terms of fluxes q_1 and n

$$\begin{aligned}
\sigma_s &= q_1\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \frac{(\mu_1 - \mu_2)n + (T_1 - T_2)s_1 n}{T_2} - \frac{p}{T_2} \\
&= \frac{(\eta_C - \eta)q_1 + (\beta_C - \beta)n}{T_2}
\end{aligned} \tag{32}$$

Eqs. (11) and (14) yield in terms of other fluxes and corresponding efficiencies,

$$\begin{aligned}
\sigma_s &= Q_1\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \frac{(\mu_1 - \mu_2)n}{T_2} - \frac{p}{T_2} \\
&= \frac{(\eta_C - \eta)Q_1 + (\zeta_C - \zeta)n}{T_2} = \frac{(\eta_C - \eta)Q_1 + (\omega_C - \omega)G_1}{T_2}
\end{aligned} \tag{33}$$

Eqs. (32) and (33) generalize to the non-isothermal case an earlier result limited to isothermal situations [1]. They show that, modulo to the multiplier $(T_2)^{-1}$, the isothermal component of the entropy production is the product of the total active flux and the deviation of chemical efficiency ζ from the corresponding efficiency of the reversible process, ζ_C. Yet, as shown by Eq. (33), the entropy production formula of an non-isothermal process contains the second (thermal) component equal to the product of total (i.e. mass transfer including) heat flux $Q_1 \equiv q_1 + T_1 s_1 n$ and the deviation of thermal efficiency η from the Carnot efficiency.

The subscript C points out that the reversible efficiencies η_C, ζ_C and ω_C refer to the so-called Carnot point of the system, also called "open circuit point" [2]. This point is associated with vanishing currents and upper, reversible limits for thermal and chemical efficiencies.

5. Dissipative availabilities in dynamical systems

As resources are finite by nature, in real systems only the second fluid constitutes an infinite constant reservoir (e.g. an environment), whereas the first fluid (a resource) changes its properties when it proceeds through stages in time. We have to attribute changes in state variables to each considered flux.

For the mass flux, which equals $G_{1'}/\mu_{1'}$, the suitable state coordinate is the invariant amount of reacting substance $N = N_{1'} = N_{2'}$

or the concentration $X = N/I$. For the entropy flux, $Q_{1'}/T_{1'}$, the state variable is the entropy S. In the formulae below we use symbols S and T for the variable entropy $S_1(t)$ and temperature $T_1(t)$ in the bulk of the resource fluid. For an endoreversible process the yield of the specific work at flow in terms of the Carnot controls is

$$\begin{aligned} W \equiv P/I &= -\int_{T^{\mathrm{i}},\mu^{\mathrm{i}}}^{T^{\mathrm{f}},\mu^{\mathrm{f}}} \{(T' - T_2)\mathrm{d}S + (\mu' - \mu_2)\mathrm{d}N\} \\ &= -\int_{T^{\mathrm{i}},\mu^{\mathrm{i}}}^{T^{\mathrm{f}},\mu^{\mathrm{f}}} \{(T - T_2)\mathrm{d}S + (\mu - \mu_2)\mathrm{d}N\} \\ &\quad -\int_{T^{\mathrm{i}},\mu^{\mathrm{i}}}^{T^{\mathrm{f}},\mu^{\mathrm{f}}} \{(T' - T)\mathrm{d}S + (\mu' - \mu)\mathrm{d}N\} \end{aligned} \tag{34}$$

In the second line the first integral is the reversible work, whereas the second integral is the lost work. When the subscript 2 refers to the state of environment, Eq. (29) leads to a generalized or finite time exergy $A = \max W$ satisfying the formula

$$\begin{aligned} A &= \max W \equiv \max(P/I) \\ &= \max \int_{T^{\mathrm{i}},\mu^{\mathrm{i}}}^{T^{\mathrm{f}},\mu^{\mathrm{f}}} \{-(T - T_2)\mathrm{d}S - (\mu - \mu_2)\mathrm{d}N\} \\ &= H^{\mathrm{i}} - H^{\mathrm{f}} - T_2(S^{\mathrm{i}} - S^{\mathrm{f}}) - \mu_2(N^{\mathrm{i}} - N^{\mathrm{f}}) \\ &\quad - \min \int_{T^{\mathrm{i}},\mu^{\mathrm{i}}}^{T^{\mathrm{f}},\mu^{\mathrm{f}}} \{(T' - T)\mathrm{d}S + (\mu' - \mu)\mathrm{d}N\} \end{aligned} \tag{35}$$

Eq. (35) expresses – in terms of Carnot controls – the Gouy–Stodola law for the endoreversible system, cf. [15,16]. In terms of the Carnot controls the thermodynamic form of the lost work expression (without kinetics incorporated) is classical, and it is the sum of products of thermodynamic fluxes and forces:

$$T_2 S_\sigma = \int_{T_{\mathrm{i}}}^{T_{\mathrm{f}}} \{(T' - T)\dot{S} + (\mu' - \mu)\dot{N}\}\mathrm{d}\tau \tag{36}$$

As shown by Eq. (35) the maximum work produced by the engine equals to the change of the classical exergy reduced by the lost work or the product of the reservoir's temperature and the (minimum) entropy production. This expresses, of course, the Gouy–Stodola law which links the lost work with the entropy generation. An analogous equation is obtained for the power consumer, but then the effect of entropy production is added to the classical exergy change, i.e. an increase of work input is necessary to assure the required state change in a finite time.

Eq. (35) defines the "endoreversible" limit for the work production between two given states and for a given number of transfer units. Even this simple limit is stronger than that the one predicted by the classical exergy. What can be said about a yet stronger limit which involves an internal dissipation in the participating thermal machine? We need to consider the hierarchy of limits. For limits of higher rank, an internal entropy generation is included in the dissipation model and then Eq. (35) is replaced by its simple generalization which contains the sum of the "endoreversible" and "internal" productions of the entropy, $S_\sigma^{\mathrm{endo}} + S_\sigma^{\mathrm{int}}$, in agreement with the Gouy–Stodola law. In general, extra components of total entropy source are included at the expense of a more detailed information input, 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 the cost of the related information is 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 A and real work W_{real} that are valid in the form $W_{\mathrm{real}} > \Delta A_k > \Delta A_1 > \Delta A_0$, where ΔA_1 refers to the change of "endoreversible exergy", and ΔA_0 pertains to the change of the classical exergy. The classical exergy change constitutes then the weakest or the worst standardized limit on the real work. In the described scheme any considerations of relations between the irreversibility and costs are unnecessary.

6. Characteristics of steady isothermal engines

Expressing chemical potentials

$$\mu_k = \mu_{0k} + RT\ln x_k = \mu_{0k} + RT\ln(X_k/1 + X_k) \tag{37}$$

in terms of molar fraction of the active component in "upper" and "lower" part of the system ($k = 1,2$), we obtain the affinity-related efficiency (23) in the form

$$\zeta = \mu_{1'} - \mu_{2'} = \zeta_0 + RT\ln\left(\frac{x_{1'}}{x_{2'}}\right) \equiv \zeta_0 + RT\ln\left(\frac{X_{1'}(1 + X_{2'})}{X_{2'}(1 + X_{1'})}\right) \tag{38}$$

where

$$\zeta_0 = \mu_{01'} - \mu_{02'} = \mu_{01} - \mu_{02} \tag{39}$$

The last equation applies the property of chemical passivity for each component in the chemically inactive parts of the system, where only diffusive transport takes place. The equation describes, in fact, the standard Gibbs energy for the isomerisation reaction considered. The constant ζ_0 involves chemical potentials of substrate and product in their reference states. The reference value ζ_0 vanishes only if both components are identical. In general, however, the constant ζ_0 is non-vanishing.

When both reservoirs are infinite the process is at the steady-state. The mass transfer between each reservoir and the production section of the system is described by certain kinetic equations. For simplicity, we assume that these equations are linear. The mass balances for the substance transferred, produced and consumed are contained in the equations

$$n = g_1(x_1 - x_{1'}) \tag{40}$$

and

$$n = g_2(x_{2'} - x_2) \tag{41}$$

In order to determine work characteristics of the chemical engine at the steady-state (unlimited stock of fuel) one searches for concentrations $x_{1'}$ and $x_{2'}$ expressed in terms of a control variable. For the chemical engine a suitable quantity can be efficiency ζ, Eqs. (38) and (39). This means that the following system of equations should be solved

$$\zeta = \zeta_0 + RT\ln\left(\frac{x_{1'}}{x_{2'}}\right) \tag{42}$$

$$g_1(x_1 - x_{1'}) = g_2(x_{2'} - x_2) = n \tag{43}$$

From the first equation of this set we find

$$\frac{x_{2'}}{x_{1'}} = \exp\left(-\frac{\zeta - \zeta_0}{RT}\right) \tag{44}$$

Substituting $x_{2'}$ from this equation to the first equality of Eq. (43) written in the form

$$g_1 x_{1'} + g_2 x_{2'} = g_1 x_1 + g_2 x_2 \tag{45}$$

one obtains

$$x_{1'} = \frac{g_1 x_1 + g_2 x_2}{g_1 + g_2\exp\left(-\frac{\zeta - \zeta_0}{RT}\right)} \tag{46}$$

and

$$x_{2'} = \frac{g_1 x_1 + g_2 x_2}{g_1 + g_2\exp\left(-\frac{\zeta - \zeta_0}{RT}\right)}\exp\left(-\frac{\zeta - \zeta_0}{RT}\right) = \frac{g_1 x_1 + g_2 x_2}{g_1\frac{\zeta - \zeta_0}{RT} + g_2} \tag{47}$$

Each of the last two equations can be used in the balance-kinetic formula (43). This leads to an equation describing the feed flux of the active component of fuel in terms of chemical efficiency

$$n = g_1x_1 - g_1x_{1'} = g_1x_1 - g_1\frac{g_1x_1 + g_2x_2}{g_1 + g_2\exp\left(-\frac{\zeta-\zeta_0}{RT}\right)} \tag{48}$$

This equation can be yet simplified into the form

$$\begin{aligned} n &= g_1(x_1 - x_{1'}) = g_1g_2\frac{x_1\exp\left(-\frac{\zeta-\zeta_0}{RT}\right) - x_2}{g_1 + g_2\exp\left(-\frac{\zeta-\zeta_0}{RT}\right)} \\ &= g_1g_2\frac{x_1 - x_2\exp\left(\frac{\zeta-\zeta_0}{RT}\right)}{g_1\exp\left(\frac{\zeta-\zeta_0}{RT}\right) + g_2} \end{aligned} \tag{49}$$

Thus, the feed rate of the system by the active reactant can be described by two equivalent expressions

$$n = \frac{x_1 - x_2\exp\left(\frac{\zeta-\zeta_0}{RT}\right)}{(g_1)^{-1} + (g_2)^{-1}\exp\left(\frac{\zeta-\zeta_0}{RT}\right)} \tag{50}$$

or

$$\frac{n}{g_1} = \frac{x_1 - x_2\exp\left(\frac{\zeta-\zeta_0}{RT}\right)}{1 + (g_1/g_2)\exp\left(\frac{\zeta-\zeta_0}{RT}\right)} \tag{51}$$

The function inverse to the above defines the chemical efficiency in terms of the reactant's feed rate n

$$\zeta = \zeta_0 + RT\ln\left(\frac{x_1 - ng_1^{-1}}{ng_1^{-1}(g_1/g_2) + x_2}\right) \tag{52}$$

This equation shows that an effective concentration of the reactant in the upper reservoir $x_{1\mathrm{eff}} = x_1 - g_1^{-1}n$ is decreased, whereas an effective concentration of the product in the lower reservoir $x_{2\mathrm{eff}} = x_2 + g_2^{-1}n$ is increased due to the finite mass flux. Consequently, the efficiency ζ decreases nonlinearly with n. When the effect of the resistance g_k^{-1} is ignorable or the flux n is very small, reversible efficiency, ζ_C, is attained. Quite generally the power function described by the product $\zeta(n)n$ exhibits the maximum power for a finite value of the flux n.

Eqs. (4) and (50) yield power in terms of efficiency ζ of an isothermal process

$$p = (\mu_{1'} - \mu_{2'})n = \zeta\frac{x_1 - x_2\exp\left(\frac{\zeta-\zeta_0}{RT}\right)}{(g_1)^{-1} + (g_2)^{-1}\exp\left(\frac{\zeta-\zeta_0}{RT}\right)} \tag{53}$$

This power function exhibits a maximum for a certain efficiency, ζ, this efficiency being a chemical analogue of the well known Chambadal–Novikov–Curzon–Ahlborn efficiency (*CNCA* efficiency [2,12]). The maximum power can be considered with respect to control variables n and ζ, for example. Yet, other control variables can be considered.

Similarly like in heat processes, for which the Carnot temperature was applied as a suitable control [4,14], we can use the Carnot chemical potential, μ'. For an isothermal process Carnot chemical potential μ' may be obtained from the invariance of the chemical efficiency

$$\mu_{1'} - \mu_{2'} = \mu' - \mu_2 \tag{54}$$

Therefore,

$$\mu' = \mu_2 + \mu_{1'} - \mu_{2'} = \mu_2 + \zeta \tag{55}$$

The structure of μ' may be more involved in non-isothermal processes when the classical definition of heat flux is applied. However for the *generalized* heat flux, $Q_{1'} \equiv q_{1'} + T_{1'}s_{1'}n$, Carnot chemical potential μ' represented by Eq. (55) remains valid even in non-isothermal cases. Chemical efficiency of any (isothermal or not) process of energy generation expressed in terms of μ' is then $\zeta = p/n = \mu' - \mu_2$.

The quantity μ' can thus be a process control suitable in considerations of the connection between the rate change of the resource potential and the process driving force. Whenever $\mu' = \mu_1$ the process rate vanishes, and equations of classical thermodynamics are sufficient to characterize the system. For $\mu' < \mu_1$ the driving reactant (fuel) is consumed in the upper reservoir, its chemical potential μ_1 decreases gradually, and the system produces power. In the opposite case, when $\mu' > \mu_1$, the system consumes power for the purpose of the resource utilization, to increase its chemical potential. These properties are valid regardless of particular structure of kinetic equations (linear or not).

At the Carnot point (also called "open circuit point of the system" [2]), rates and power vanish and the system efficiency ζ attains its upper limit. Only then is this efficiency identical with the reversible chemical affinity of the reaction. For our model

$$\zeta_C = p/n = \mu_1 - \mu_2 \tag{56}$$

Putting Eq. (50) or (51) to zero yields

$$x_1 = x_2\exp\left(\frac{\zeta_C - \zeta_0}{RT}\right) \tag{57}$$

This formula leads to the limiting reversible efficiency in the form determined by the chemical affinity of reaction at the reversible Carnot point

$$\zeta_C = \zeta_0 + RT\ln\left(\frac{x_1}{x_2}\right) \equiv A_C \tag{58}$$

However, the power produced at the "open circuit" state equals zero, corresponding with vanishing feed flux of the driving reactant.

Intensity of the entropy generation in the system, Eq. (33), can be presented in several forms. For the isothermal system considered three forms of σ_s can be discussed. In the first, the controlling quantity is the efficiency ζ

$$\sigma_s = \frac{(\zeta_C - \zeta)n}{T} = \frac{(\zeta_C - \zeta)}{T}\left(\frac{x_1 - x_2\exp\left(\frac{\zeta-\zeta_0}{RT}\right)}{(g_1)^{-1} + (g_2)^{-1}\exp\left(\frac{\zeta-\zeta_0}{RT}\right)}\right) \tag{59}$$

In the second, the control variable is Carnot chemical potential

$$\begin{aligned} \sigma_s &= \frac{((\mu_1 - \mu_2) - (\mu' - \mu_2))n}{T} \\ &= \frac{(\mu_1 - \mu')}{T}\frac{\left(x_1 - x_2\exp\left(\frac{\mu'-\mu_2-\zeta_0}{RT}\right)\right)}{(g_1)^{-1} + (g_2)^{-1}\exp\left(\frac{\mu'-\mu_2-\zeta_0}{RT}\right)} \end{aligned} \tag{60}$$

In the third form the control is the fuel flux n; then, from Eq. (52),

$$\sigma_s = \frac{(\zeta_C - \zeta)n}{T} = R\ln\left(\left(\frac{x_1}{x_2}\right)\left(\frac{ng_2^{-1} + x_2}{x_1 - ng_1^{-1}}\right)\right) \tag{61}$$

In the so-called "short circuit point", there is no power production for any value of ζ_0, despite possible chemical reaction. Only entropy is then produced with a maximum intensity

$$\begin{aligned} \sigma_{s_{sc}} &= \frac{\zeta_C}{T}\left(\frac{x_1 - x_2\exp\left(\frac{-\zeta_0}{RT}\right)}{(g_1)^{-1} + (g_2)^{-1}\exp\left(\frac{-\zeta_0}{RT}\right)}\right) \\ &= \frac{(\mu_1 - \mu_2)}{T}\frac{\left(x_1 - x_2\exp\left(\frac{-\zeta_0}{RT}\right)\right)}{(g_1)^{-1} + (g_2)^{-1}\exp\left(\frac{-\zeta_0}{RT}\right)} \end{aligned} \tag{62}$$

When $\zeta_0 = 0$ the entropy production at the "short circuit point" corresponds with the situation without chemical reaction and energy generation

$$\begin{aligned} (\sigma_s)_{\zeta_0=0} &= \frac{\zeta_C n_{zw}}{T} = \frac{\zeta_C}{T}\left(\frac{x_1 - x_2}{(g_1)^{-1} + (g_2)^{-1}}\right) \\ &= T^{-1}\frac{(\mu_1 - \mu_2)(x_1 - x_2)}{(g_1)^{-1} + (g_2)^{-1}} \end{aligned} \tag{63}$$

Clearly, only at the short circuit point and for the associated absence of power yield the entropy production at this point (modulo to multiplier T^{-1}) is equal to the product of the reaction rate and its chemical affinity. This is the classical result, which, however, does not hold when the system produces power (i.e. belongs to the class of “active systems”).

Assuming a finite ζ_0, we determine the rate of the system feed by the active reactant in two alternative forms. The first one describes the feed flux n in terms of ζ, whereas the second – in terms of μ'

$$n = \frac{x_1 - x_2 \exp\left(\frac{\zeta-\zeta_0}{RT}\right)}{(g_1)^{-1} + (g_2)^{-1}\exp\left(\frac{\zeta-\zeta_0}{RT}\right)} = \frac{x_1 - x_2 \exp\left(\frac{\mu'-\mu_2-\zeta_0}{RT}\right)}{(g_1)^{-1} + (g_2)^{-1}\exp\left(\frac{\mu'-\mu_2-\zeta_0}{RT}\right)} \tag{64}$$

Power produced in the reactor may be determined in three forms, as a function of ζ, in terms of μ' or as a function of n. The first two forms are described by an equation

$$\begin{aligned} p = (\mu_{1'} - \mu_{2'})n &= \zeta \frac{x_1 - x_2 \exp\left(\frac{\zeta-\zeta_0}{RT}\right)}{(g_1)^{-1} + (g_2)^{-1}\exp\left(\frac{\zeta-\zeta_0}{RT}\right)} \\ &= \frac{(\mu' - \mu_2)\left(x_1 - x_2 \exp\left(\frac{\mu'-\mu_2-\zeta_0}{RT}\right)\right)}{(g_1)^{-1} + (g_2)^{-1}\exp\left(\frac{\mu'-\mu_2-\zeta_0}{RT}\right)} \end{aligned} \tag{65}$$

Using inverse function $\zeta(n)$, Eq. (52), one may describe power in terms of the reagent flux n

$$p = \zeta(n)n = \zeta_0 n + RTn \ln\left(\frac{x_1 - ng_1^{-1}}{ng_2^{-1} + x_2}\right) \tag{66}$$

Eq. (52) proves that efficiency ζ decreases nonlinearly with feed flux n. The consequence of this property is the maximum of the product $\zeta(n)n$ describing the power yield. The maximum power point is the result of maximizing of the power function with respect to its free control variable, ζ, μ' or n. Analytical methods are seldom effective. However, one can use diagrams describing functions $p(\zeta)$, $p(\mu')$ or $p(n)$ to determine the maximum point graphically. Information regarding the location of maximum point can also be obtained by a numerical search.

System characteristics in terms of control μ' are presented in Figs. 2 and 3.

Eq. (66) shows that a maximum of power p is attained for a fuel flux n satisfying an equation

$$\frac{\mathrm{d}p}{\mathrm{d}n} = \zeta_0 + RT\ln\left(\frac{x_1 - ng_1^{-1}}{ng_2^{-1} + x_2}\right) - RTn\frac{g_1^{-1}x_2 + g_2^{-1}x_1}{(x_1 - ng_1^{-1})(ng_2^{-1} + x_2)} = 0 \tag{67}$$

Its numerical solution generates a function describing the optimal feed of the system by the active reactant

$$n_{\mathrm{mp}} = f(\zeta_0, T, x_1, x_2, g_1, g_2) \tag{68}$$

Substituting this result into Eq. (26), leads to the chemical counterpart of the Chambadal–Novikov–Curzon–Ahlborn efficiency (CNCA efficiency; [2,12]). It describes the efficiency ζ_{mp} of the chemical engine at the maximum power point in terms of the system properties

$$\zeta_{\mathrm{mp}} = f(\zeta_0, T, x_1, x_2, g_1, g_2) \tag{69}$$

The curve of produced power has two zero points. The first is the “short circuit point” (also the point of vanishing efficiency), and, the second is the “open circuit point” or Carnot point at which the feed of the system with the active component is infinitely slow. Eq. (50) proves that the feed rate of the active reagent in the short circuit point (where $\zeta = 0$) is

$$n_{\mathrm{zw}} = \frac{x_1 - x_2 \exp\left(\frac{-\zeta_0}{RT}\right)}{(g_1)^{-1} + (g_2)^{-1}\exp\left(\frac{-\zeta_0}{RT}\right)} \tag{70}$$

For a non-vanishing $\zeta_0 = \mu_{01'} - \mu_{02'} = \mu_{01} - \mu_{02}$, the short circuit point corresponds with a particular, “purely dissipative” state of the system at which lossy elements predominate so significantly that the chemical reaction does not produce any power, despite of non-vanishing reaction rate and existing finite potential of ζ_0 (but not ζ) for the production of this power. For $\zeta_0 = 0$ the discussed equation describes the situation, in which the reactor does not exist, the fuel stream flows by two sequentially connected conductors, and molar flux of the reactant, n, is determined by the specification of the overall conductance $g = ((g_1)^{-1} + (g_2)^{-1})^{-1}$. Consequently, for $\zeta_0 = 0$ and at the short circuit point of the system

$$n_{\mathrm{zw}} = \frac{x_1 - x_2}{(g_1)^{-1} + (g_2)^{-1}} \tag{71}$$

7. Sequential models for dynamic power generators

When resources are limited their quality decreases in time, and dynamical processes arise. Power optimization requires then variational methods to maximize power integrals subject to process differential constraints. Taking into account analytical difficulties we often apply methods of discrete optimization, e.g. the dynamic programming method. An extremum problem for a power integral is then broken down into an optimization problem for a cascade with a finite number of stages.

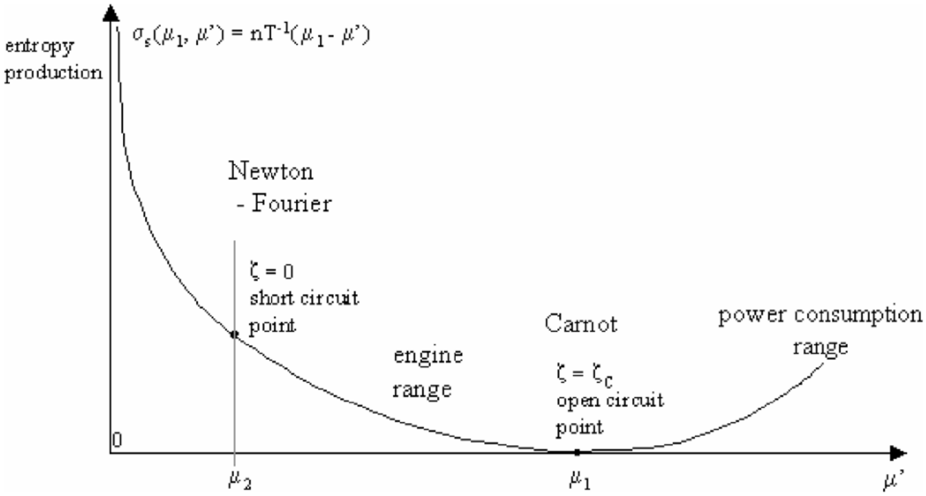

Fig. 2. Entropy generation in the engine in terms of Carnot chemical potential μ' as a control variable.

7.1. Discrete models

Regarding computer needs, we shall now introduce a suitable discrete model of the chemical engine. We consider the optimal fuel consumption in a cascade of K engines, with efficiency ζ^k or local feed n^k as control variables at kth stage. We also test Carnot chemical potentials μ'^k as possible controls. To describe fuel consumption we exploit the mass balance. Some suitable notions are introduced first.

Let us introduce a cumulative flux of active reactant over the first k stages of the cascade, $N^k = \Sigma n^l$, where $l = 1,2,\ldots,k$. The sequence of local fluxes n^l (characterized by "upper" potentials μ_1^k in the kth stage engine) describes allocations of N^k between stages $1,2,\ldots,k$. Each local flux n^k of the active reagent at stage k equals the change of cumulative mass flux $N^k - N^{k-1}$.

The mass balance at the stage k

$$n^k \equiv N^k - N^{k-1} = -I(X_1^k - X_1^{k-1}) = -Ic_m(\mu_1^k - \mu_1^{k-1}) \tag{72}$$

shows that the local molar flux at the stage k (an interval of the cumulative mass flux N^k) can be evaluated as the (negative) product of molar flux of inert, I, and the change of reactant's concentration, ΔX^k. Mass capacity c_m can be introduced as the partial derivative of the concentration X with respect to the chemical potential at the constant temperature. Then, in the case of an isothermal mass exchange, any change in the cumulative coordinate N can be evaluated in terms of the reactant's chemical potential.

The reactant's flux n^k can be eliminated on account of difference $X_1^k - X_1^{k-1}$ with the help of Eq. (72). Simultaneously it is convenient to have at our disposal a separate expression for efficiency ζ^k in terms of concentrations X_1^k and X_1^{k-1}. Both these needs are satisfied in one stroke below. Mass balance (72) and the current-efficiency characteristic (51) yield an expression

$$\begin{aligned}-I(X_1^k - X_1^{k-1}) &= N_1^k - N_1^{k-1}\\ &= \frac{x_1 - x_2\exp\left(\frac{\zeta-\zeta_0}{RT}\right)}{1+(g_1/g_2)\exp\left(\frac{\zeta-\zeta_0}{RT}\right)}\beta_1'^k(A^k - A^{k-1})\end{aligned} \tag{73}$$

where $\beta_1' \equiv \beta_1 y = \beta_1 a_1/(a_1 + a_2)$ and $\beta_1'^k(A^k - A^{k-1}) = g_1^k$. Whence

$$-\frac{I(X_1^k - X_1^{k-1})}{\beta_1'^k(A^k - A^{k-1})} \equiv \frac{n^k}{g_1^k} = \frac{x_1 - x_2\exp\left(\frac{\zeta-\zeta_0}{RT}\right)}{1+(g_1/g_2)\exp\left(\frac{\zeta-\zeta_0}{RT}\right)} \tag{74}$$

Since the inversion of Eq. (51), i.e. the right hand side of Eq. (77), is Eq. (52)

$$\zeta = \zeta_0 + RT\ln\left(\frac{x_1 - ng_1^{-1}}{ng_1^{-1}(g_1/g_2) + x_2}\right) \tag{52}$$

the chemical efficiency ζ^k in terms of X_1^k and X_1^{k-1} is

$$\zeta^k = \zeta_0^k + RT\ln\left(\frac{\frac{X_1^k}{1+X_1^k} + \frac{I(X_1^k - X_1^{k-1})}{\beta_1'^k a_v^k F^k(l^k - l^{k-1})}}{-\frac{I(X_1^k - X_1^{k-1})}{\beta_1'^k a_v^k F^k(l^k - l^{k-1})}\left(\frac{g_1}{g_2}\right) + x_2}\right) \tag{75}$$

In the engine mode the concentration of the active reactant can only decrease along a path, thus the term with the discrete slope $\Delta X^k/\Delta l$ in Eq. (75) is negative. Consequently, the efficiency of a stage working in the engine mode is lower than the Carnot efficiency.

The quantity

$$\frac{I}{\beta_1' a_v F} \equiv H_{\mathrm{TU}_1} \tag{76}$$

has units of length, and is known from the mass transfer theory as the "height of the mass transfer unit" (H_{TU}). In Eq. (76) it is referred to partial mass transfer coefficient of active reactant, β_1', although an analogous quantity could be defined for the product. The non-dimensional length

$$\tau_1 \equiv l/H_{\mathrm{TU}_1} \tag{77}$$

is identical with the "number of transfer units" N_{TU} for mass transfer. Since it is proportional to the system's extent l and hence to the contact time of active reactant with mass exchange area, it also plays the role of a non-dimensional time, and this is why it is designated by τ_1

$$\frac{p^k}{I} = -\left\{\zeta_0 + RT\ln\left(\frac{\frac{X_1^k}{1+X_1^k} + \frac{X_1^k - X_1^{k-1}}{\tau_1^k - \tau_1^{k-1}}}{x_2 - j\frac{X_1^k - X_1^{k-1}}{\tau_1^k - \tau_1^{k-1}}}\right)\right\}(X_1^k - X_1^{k-1}) \tag{78}$$

The conductance ratio is defined as coefficient $j \equiv g_1/g_2$.

The total power delivered from the N-stage process per unit flux of the inert is the sum of contributions of stages. This sum is a discrete functional which is maximized by the suitable choice of the interstage concentrations and allocation of time intervals between the stages.

$$\begin{aligned}W^N &\equiv \sum_{k=1}^{N} w^k\\ &= -\sum_{k=1}^{N}\left\{\zeta_0 + RT\ln\left(\frac{\frac{X_1^k}{1+X_1^k} + \frac{X_1^k - X_1^{k-1}}{\tau_1^k - \tau_1^{k-1}}}{x_2 - j\frac{X_1^k - X_1^{k-1}}{\tau_1^k - \tau_1^{k-1}}}\right)\right\}(X_1^k - X_1^{k-1})\end{aligned} \tag{79}$$

7.2. Continuous models

Models of continuous systems producing power are obtained as limits of models of suitable discrete systems for number of stages approaching infinity. An example is the continuous limit describing an integral of total power per unit molar flow of the inert

$$W = -\int_{\tau_1^i}^{\tau_1^f}\left\{\zeta_0 + RT\ln\left(\frac{\frac{X}{1+X} + \frac{dX}{d\tau_1}}{x_2 - j\frac{dX}{d\tau_1}}\right)\right\}\frac{dX}{d\tau_1}d\tau_1 \tag{80}$$

The continuous variable X plays here the same role as the discrete variable X_1^k in Eq. (79). Eqs. (79) and (80) represent respectively discrete and continuous Lagrange descriptions of the optimized process.

We can also apply controls that are certain state variables, and have no interpretation of rates. For example, using Carnot chemical potential $\mu' = \mu_2 + \zeta$ in integral (80) we obtain

$$W = -\int_{\tau_1^i}^{\tau_1^f}\zeta\frac{dX}{d\tau_1}d\tau_1 = -\int_{\tau_1^i}^{\tau_1^f}(\mu' - \mu_2)\frac{dX}{d\tau_1}d\tau_1 \tag{81}$$

where μ' satisfies an equation

$$\mu' = \mu_2 + \zeta_0 + RT\ln\left(\frac{\frac{X}{1+X} + \frac{dX}{d\tau_1}}{x_2 - j\frac{dX}{d\tau_1}}\right) \tag{82}$$

Its solution with respect to the time derivative yields

$$\frac{dX}{d\tau_1} = -\frac{\frac{X}{1+X} - x_2\exp\left(\frac{\mu'-\mu_2-\zeta_0}{RT}\right)}{1 + j\exp\left(\frac{\mu'-\mu_2-\zeta_0}{RT}\right)} \tag{83}$$

Using in this formula an expression linking molar fraction $x = X/(1 + X)$ with chemical potential

$$\frac{X}{1+X} = \exp\left(\frac{\mu - \mu_{0_1}}{RT}\right) \tag{84}$$

and introducing mass capacity $c_m(\mu)$

$$c_m(\mu) \equiv \frac{dX}{d\mu} = \frac{1}{RT}\frac{\exp\left(\frac{\mu-\mu_{0_1}}{RT}\right)}{\left(1 - \exp\left(\frac{\mu-\mu_{0_1}}{RT}\right)\right)^2} \tag{85}$$

we obtain a nonlinear equation of process dynamics in terms of the chemical potential of the active component of fuel

$$c_m(\mu)\frac{\mathrm{d}\mu}{\mathrm{d}\tau_1} = -\frac{\exp\left(\frac{\mu-\mu_{0_1}}{RT}\right) - x_2\exp\left(\frac{\mu'-\mu_2-\zeta_0}{RT}\right)}{1 + j\exp\left(\frac{\mu'-\mu_2-\zeta_0}{RT}\right)} \tag{86}$$

A corresponding power formula has the form

$$W = \int_{\tau_1^{\mathrm{i}}}^{\tau_1^{\mathrm{f}}} (\mu' - \mu_2)\frac{\exp\left(\frac{\mu-\mu_{0_1}}{RT}\right) - x_2\exp\left(\frac{\mu'-\mu_2-\zeta_0}{RT}\right)}{1 + j\exp\left(\frac{\mu'-\mu_2-\zeta_0}{RT}\right)}\mathrm{d}\tau_1 \tag{87}$$

Dynamical optimization tackles integral (87) subject to differential constraint (86). The mathematical structure of the power integral and constraint is here much more complicated than in the respective heat problem, where use of the Carnot representation assured a simplest formal structure of the mathematical problem, see [15–18] and Appendix. This also substantiates use of numerical methods.

8. A computational algorithm for dynamical process with power maximization

We shall now describe a computational algorithm in which the discrete problem of maximum power is treated as an optimal control problem, and a suitable control variable is chosen to assure a relatively simple model. The simplicity condition is satisfied by a simple link of control with rate change of reactant's concentration in the fuel, $\mathrm{d}X/\mathrm{d}\tau_1$. In the discrete version this rate is replaced by the difference ratio $\Delta X/\Delta\tau_1$.

We introduce a control variable describing the fuel consumption

$$v^k \equiv -\frac{n^k}{g_1} \tag{88}$$

It is negative in engine modes and positive in power consumption modes. Under the assumption of Lewis analogy we may write

$$v \equiv -\frac{n}{g_1} = -\frac{N^k - N^{k-1}}{\gamma_1^k - \gamma_1^{k-1}} = \frac{I(X_1^k - X_1^{k-1})}{\beta_1'^k(A_1^k - A_1^{k-1})} = \frac{X_1^k - X_1^{k-1}}{\tau_1^k - \tau_1^{k-1}} \tag{89}$$

$$u \equiv -\frac{q_1}{g_1} = -\frac{Q^k - Q^{k-1}}{\gamma_1^k - \gamma_1^{k-1}} = \frac{Ic(T_1^k - T_1^{k-1})}{\alpha_1'^k(A_1^k - A_1^{k-1})} = \frac{T_1^k - T_1^{k-1}}{\tau_1^k - \tau_1^{k-1}} \tag{90}$$

The optimization problem searches for a maximum of the performance index

$$W^N = -\sum_{k=1}^{N}\left\{\zeta_0 + RT^k\ln\left(\frac{X_1^k(1+X_1^k)^{-1} + v^k}{x_2 - jv^k}\right)\right\}v^k\theta^k \tag{91}$$

($j \equiv g_1/g_2$) subject to difference constraints

$$X_1^k - X_1^{k-1} = v^k\theta^k \tag{92}$$

$$\tau_1^k - \tau_1^{k-1} = \theta^k \tag{93}$$

In a non-isothermal problem an extra equation has to be included to treat temperature changes

$$T_1^k - T_1^{k-1} = u^k\theta^k \tag{94}$$

and the power function has to be enlarged to include the thermal component of power yield. Some information related to the thermal component is given in Appendix.

Change in the sign of performance function (91) transforms the problem into a discrete problem of power minimization, whose numerical solution is outlined below.

We apply the method of dynamic programming which searches for a solution of Bellman's recurrence equation. A general form of this equation is

$$R^n(\mathbf{x}^n, t^n) = \min_{\mathbf{u}^n,\theta^n}\{l_0^n(\mathbf{x}^n, t^n, \mathbf{u}^n, \theta^n)\theta^n + R^{n-1}(\mathbf{x}^n - \mathbf{f}^n(\mathbf{x}^n, t^n, \mathbf{u}^n, \theta^n)\theta^n, t^n - \theta^n)\} \tag{95}$$

where $R^n(\mathbf{x}^n, t^n) = \min(-W^n)$ is the function describing the minimum of power consumed. This is a function of optimal cost type. In an isothermal case $\mathbf{x} = X_1$, $\mathbf{u} = v$, and $t = \tau$.

Applying Eq. (95) to the isothermal problem described by Eqs. (91)–(93), the following recurrence equation is obtained

$$R^k(X^k, \tau^k) = \min_{\mathbf{u}^k,\ \theta^k}\left\{\left\{\zeta_0 + RT\ln\left(\frac{X_1^k(1+X_1^k)^{-1} + v^k}{x_2 - jv^k}\right)\right\}v^k\theta^k + R^{n-1}(X_1^k - \theta^n v^k, \tau^k - \theta^k)\right\} \tag{96}$$

While the analytical solving of the discrete problem (91)–(93) is a difficult task, it is quite easy to solve recurrence Eq. (96) numerically. Low dimensionality of state vector in Eq. (96) assures a decent accuracy of DP solution. Moreover, an original accuracy can significantly be improved after performing the so-called dimensionality reduction associated with the elimination of time t^k as the state variable by using a Lagrange multiplier λ. In the transformed problem, without coordinate t^k, accuracy of DP solutions is high. Section 2.3 of Ref. [15] discusses related computational issues of this sort with more detail (See Fig. 4).

The block scheme of computational process (Fig. 4) is discussed in [1], where the system state is represented by concentration of active component of fuel, X_1^k, as in Eq. (96).

For a continuous isothermal process with constant coefficients g_1,g_2,j,..., an analytical condition associated with the power optimum or Eq. (96) can be determined in the form of constancy of an energy-like function along an optimum path. This energy-like function, is, in fact, the Hamiltonian of the power optimization problem, that is expressed here in terms of rates rather than adjoint variables (the latter being the natural variables of the Hamiltonian). The optimality condition with respect to the rates v^k and u^k proves that the state adjoints are equal to the partial derivatives of the following Lagrangian

$$L = \zeta_0\frac{\mathrm{d}X}{\mathrm{d}\tau_1} + RT\frac{\mathrm{d}X}{\mathrm{d}\tau_1}\ln\left(\frac{\frac{X}{1+X} + \frac{\mathrm{d}X}{\mathrm{d}\tau_1}}{x_2 - j\frac{\mathrm{d}X}{\mathrm{d}\tau_1}}\right) \equiv \zeta_0\dot{X} + RT\dot{X}\ln\left(\frac{x_1(X) + \dot{X}}{x_2 - j\dot{X}}\right) \tag{97}$$

with respect to its rates $\dot{X} = \mathrm{d}X/\mathrm{d}\tau_1$ and $\dot{T} = \mathrm{d}T/\mathrm{d}\tau_1$. We have defined $x_1(X) \equiv X(1+X)^{-1}$. Eq. (97) leads to the energy-like function as the Legendre transform of Lagrangian (97).

$$H(X,\dot{X}) \equiv \frac{\partial L}{\partial\dot{X}}\dot{X} - L = RT\dot{X}^2\frac{x_2 + jx_1(X)}{(x_1(X) + \dot{X})(x_2 - j\dot{X})} \tag{98}$$

In a close vicinity of the thermodynamic equilibrium where relaxation rates are very low (close to quasistatic ones) the above optimality condition simplifies to the form

$$H(X,\dot{X}) = RT\dot{X}^2\frac{x_2 + jx_1(X)}{x_1(X)x_2} = RT\dot{X}^2\left(\frac{1+X}{X} + \frac{j}{x_2}\right) \tag{99}$$

We observe that for low rates and large concentrations X (mole fractions x_1 close to the unity) optimal relaxation rate is approximately constant in time. In an arbitrary situation, however, optimal rates $\dot{X}$ are state dependent so as to preserve the constancy of Hamiltonian (99). No constancy of chemical driving forces along the optimal path is observed.

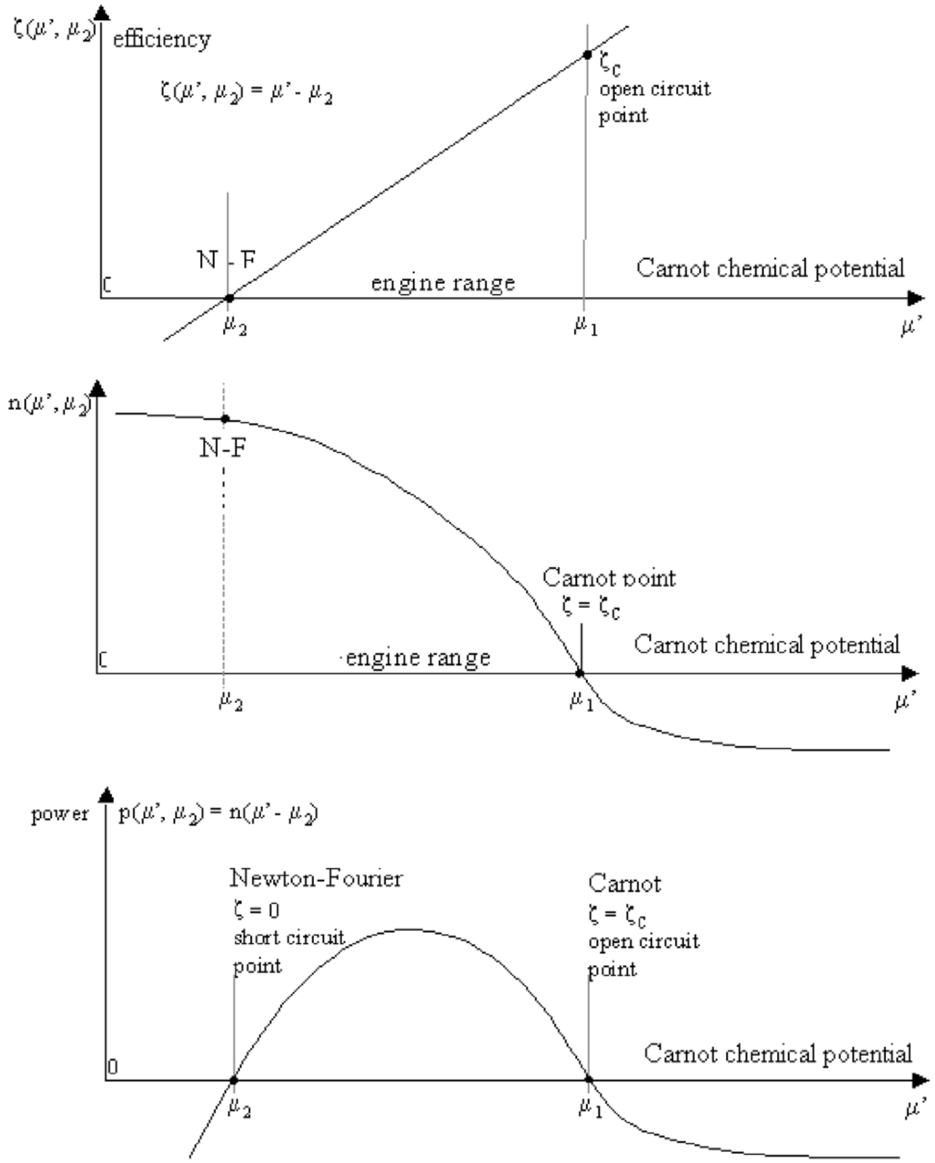

Fig. 3. Engine characteristics: efficiency, driving flux, and power yield vs. Carnot chemical potential μ'.

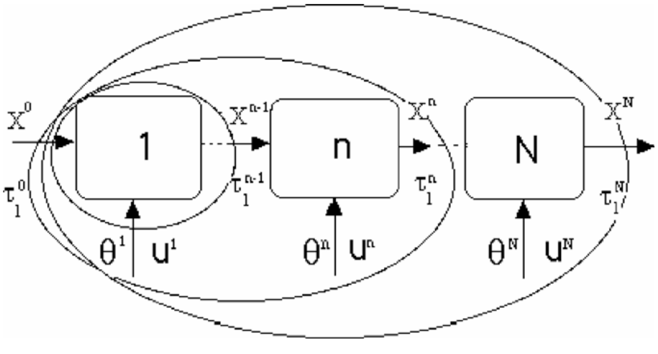

Fig. 4. Principle of multistage power generation in a dynamical chemical engine. The system stage comprizes: fuel mixture, engine and environment; at each stage mechanical power is generated. Maximized is total flux of resulting power. Control θ^n characterizes stage extent or holdup time of the fluid at the stage n, whereas control $\mathbf{u}^n$ is the fuel supply control. X^n is concentration of the active component in the fuel at stage n. In complex reaction systems coordinates of the vector of Carnot chemical potentials $\boldsymbol{\mu}'^n$ may be applied in place of concentrations $\mathbf{X}^n$.

9. Results of computations

Enhanced limits are obtained for dynamical extrema of power production or consumption in sequential chemical systems, for a finite number of steps or a finite time of resource exploitation. New results refer to the multistage production (consumption) of power in the chemical process which is driven by the diffusive transport step (Stefan diffusion through the inert) and takes into account the effect of drying out of the active component of fuel. The results of calculations for cost function $R^n(X^n, t^n) = \min(-W^N)$ show that the power limits differ for power generated and consumed, and that they depend on global working parameters of the system, e.g. total number of mass transfer units, factor of internal irreversibilities within the power generator, average process rate, number of process steps, etc. These solutions provide the design bounds for energy generators that are stronger than the familiar thermostatic bounds (i.e. classical limits for energy transformation).

As shown by the results of calculations, optimal process intensity is measured in terms of Hamiltonian H or the numerical value of Lagrange multiplier λ, an adjoint variable of the process duration. The numerical value of λ is associated with the global constraint imposed on the total holdup time or the size of the equipment. The multiplier λ is also the intensity factor whose numerical value is equal to the Hamiltonian of the power optimization problem. As such, λ is constant along an optimal trajectory of the process in which a prescribed final state is attained in a prescribed time. This constant value defines a cost of increase of the process duration by one unit. This is finally a number that should be used in calculations when the process equations are solved for an unspecified time, τ_1^N.

In the classical thermostatics, both limiting lines of thermodynamic bounds (upper bound for power produced and lower bound for power consumed) do coincide. However, the lines of classical bounds are often too far from the working regimes of real processes to make these bounds fully useful. The results obtained show the divergence of limiting lines for two basic process modes, mode of power production and mode of power consumption. They prove that the second law of thermodynamics does exclude some processes that are otherwise allowed by thermostatics. The region of the excluded processes grows for shorter process durations associated with faster mean rates and larger entropy production. Fuel holdup time and number of transfer units play an essential role. Nonlinearities and state dependence of Hamiltonian determine complex changes of chemical and thermal efficiencies and driving forces along the optimal paths of power production process.

10. Concluding remarks

Analysing the mechanical energy yield in nonlinear chemical systems we have developed an approach that uses kinetic integrals of power and provides the results of energy limits stronger than those known in classical thermodynamics. In systems with power production (engine modes) the power optimization approach performed for finite durations and finite rates leads to the decreased upper bounds, i.e, it provides lower and hence more realistic bounds for the power yield in comparison with classical thermodynamics. In systems with power consumption the power optimization approach leads to the increased lower bounds, meaning that these lower bounds are higher and hence more realistic than the lower bounds determined in classical thermodynamics (thermostatics). The enhanced nature of power limits in chemical systems constitutes a practical consequence of nontrivial implications of the second law of thermodynamics.

Also, we stress the hierarchical nature of power limits, where the "endoreversible" limits (assuming a perfect chemical generator) are one step better then those derived from the classical thermodynamics. In the analysed chemical model, the endoreversible step is just the step forward sufficient to incorporate the entropy production caused by the transport phenomena. Further steps include imperfections within the chemical generator and the effect of internal entropy production.

Finally, we point out that an *economic* problem of the system optimization and the *physical* problem of work limits for a resource, considered here, are two different problems. The real work delivered from a chemical power generator per unit time at economically optimal conditions may sometimes be much lower than the work limit associated with an appropriate consumption of fuel. In the context of work limits, the trade-off between exploitation and investment costs and the problem of investment reduction by admission of energy losses are, in fact, irrelevant issues. Also, the entropy production minimization for the chemical system considered has no relevance to the economic optimum of fuel consumption.

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Appendix. Comparison of chemical and thermal operations of power production

For comparison with Eqs. (91)–(93) we adduce below corresponding relationships describing a dynamic thermal engine. As in the main text, some formulae shall use non-dimensional time τ_1 related to partial conductance g_1, in place of more popular time τ related to the overall conductance g.

In a discrete thermal problem the performance index and constraints are

$$W^N \equiv \sum_{k=1}^{N} w^k = -c\sum_{k=1}^{N}\left\{1-\frac{T_2}{T_1^k+g_1g^{-1}u^k}\right\}u^k\theta^k \tag{A1}$$

$$T_1^k - T_1^{k-1} = u^k\theta^k \tag{A2}$$

$$\tau_1^k - \tau_1^{k-1} = \theta^k \tag{A3}$$

where W^N is the total power per unit mass flux and the bracketed expression in Eq. (A1) is the first-law efficiency. The continuous limit is an integral of power per unit mass flow

$$\begin{aligned} W &= -\int_{\tau^{\mathrm{i}}}^{\tau^{\mathrm{f}}} c\left\{1-\frac{T_2}{T+\mathrm{d}T/\mathrm{d}\tau}\right\}\left(\frac{\mathrm{d}T}{\mathrm{d}\tau}\right)\mathrm{d}\tau \\ &= -\int_{\tau^{\mathrm{i}}}^{\tau^{\mathrm{f}}} c\left\{1-\frac{T_2}{T+g_1g^{-1}\mathrm{d}T/\mathrm{d}\tau_1}\right\}\left(\frac{\mathrm{d}T}{\mathrm{d}\tau_1}\right)\mathrm{d}\tau_1 \end{aligned} \tag{A4}$$

The associated integral of entropy production is

$$S_\sigma = \int_{\tau^{\mathrm{i}}}^{\tau^{\mathrm{f}}} c\frac{(\mathrm{d}T/\mathrm{d}\tau)^2}{T(T+\mathrm{d}T/\mathrm{d}\tau)}\mathrm{d}\tau = \int_{t^{\mathrm{i}}}^{t^{\mathrm{f}}} c\frac{\chi(\mathrm{d}T/\mathrm{d}t)^2}{T(T+\chi(\mathrm{d}T/\mathrm{d}t))}\mathrm{d}t \tag{A5}$$

The temperature derivative and slope coefficients are taken here either with respect to the non-dimensional time τ (identical with the *overall* number of heat transfer units) or with the resource's holdup time t. In a periodic process of energy upgrading the latter variable represents the utilization time of a thermal resource. Both time variables are linked with length coordinate, x, by an equation

$$\tau \equiv \frac{\alpha' a_v F}{Gc}x = \frac{\alpha' a_v}{\rho c}t = \frac{t}{\chi} \tag{A6}$$

where α' is an 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 [16]. An optimal (power maximizing) relaxation process is described by a family of exponential curves [16,17]. However, in systems with nonlinear transport (e.g. in radiation engines) the relaxation curves are no longer exponential [18,19].

To apply thermal work (A1) as the additive component of isothermal chemical work (91) in agreement with Eq. (12), one should be aware of the use of approximate formulae $Q_{1'} = g_1(T_1 - T_{1'})$ and $Q_{2'} = g_2(T_{2'} - T_2)$ to describe thermal efficiency η in terms of the total heat flux (11) and effective conductances g_1, g_2 and g. Since the entropy balance of the chemical engine holds in the form $Q_{1'}/T_{1'} = Q_{2'}/T_{1'}$, the approximate thermal efficiency η in terms of $Q_{1'}$ is derived in the same way as in the case of pure heat transfer [20]. This efficiency is contained in the large braces of the second line of Eq. (A4).

Other models of dynamical chemical systems analyzed to date are available in the literature [21].

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