# Power Yield Processes: Modeling, Simulation and Optimization

P. Kuran[1,*], and S. Sieniutycz[1]

[1] *Warsaw University of Technology, Warszawa, Poland*
** Corresponding author. Tel: +48 22 8256340, Fax: +48 22 8251440, E-mail: kuran@ichip.pw.edu.pl*

**Abstract:** Classical thermodynamics is capable of determining limits on energy production or consumption in terms of the exergy change. However, they are often too distant from reality. Yet, by introducing rate dependent factors, irreversible thermodynamics offers enhanced limits that are closer to reality. Thermodynamic analyses lead to important formulas for imperfect efficiencies. In this paper power limits for generation or consumption of thermal, solar, chemical energy are obtained by application of the optimal control theory.

Power limits define maximum power released from energy generators and minimum work supplied to separators or heat pumps. In this research we consider power limits for both devices of energy generator type (engines and fuel cells) and of energy consumer type (heat pumps, separators and electrolysers). Each process is driven either by a simple heat exchange or by the simultaneous exchange of energy and mass fluxes. We stress the link of these problems with the classical problem of maximum work. Particular attention is devoted to fuel cells as electrochemical flow engines. Amongst a number of new results, notion of certain special controls (Carnot variables) plays an important role. In particular, we demonstrate their role in the analysis of heat and radiation engines, chemical power generators and fuel cells.

***Keywords:*** *efficiency, power generation, entropy, thermal machines, fuel cells.*

## Nomenclature

$A_v$ *generalized exergy per unit volume*.....$Jm^{-3}$
$a_0$ *constant related to the Stefan-Boltzmann constant*.....$Jm^{-3}K^{-4}$
$a_v$ *total area of energy exchange per unit volume*..... $m^{-1}$
$\dot{G}$ *resource flux*.....$gs^{-1}$, $mols^{-1}$
$g$ *conductance*.....$Js^{-1}K^{-a}$
$h$ *numerical value of Hamiltonian*.....$Jm^{-3}K^{-1}$
$n$ *flux of fuel reagents*.....$gs^{-1}$, $mols^{-1}$
$q$ *heat flux between a stream and pow er generator*.....$Js^{-1}$
$Q$ *total heat flux involving transferred entropies*.....$Js^{-1}$
$S_\sigma$ *entropy produced*.....$JK^{-1}$
$s_v$ *volumetric entropy*.....$J\,K^{-1}m^{-3}$
$T$ *variable temperature of resource*.....$K$
$T_{1,2}$ *bulk temperatures of reservoirs1 and 2* ...$K$
$T_{1',2'}$ *temperatures of circulating fluid*.....$K$
$T'$ *Carnot temperature control*.....$K$
$t$ *physical time*.....$s$
$W$ *work produced, positive in engine mode*...$J$
$w$ *specific work at flow or power per unit flux of a resource*.....$J/mol$
$\alpha$ *heat coefficients*..... $Jm^{-2}s^{-1}K^{-1}$
$\varepsilon$ *total energy flux*.....$Js^{-1}$
$\mu$ *chemical potential*.....$Jmol^{-1}$
$\mu'$ *Carnot chemical potential*.....$Jmol^{-1}$
$\Phi$ *factor of internal irreversibility*..... -
$\sigma$ *Stefan-Boltzmann constant*..... $Jm^{-2}\,s^{-1}K^{-4}$
$\sigma_s$ *entropy production of the system*..... $JK^{-1}s^{-1}$
$\zeta$ *chemical efficiency*..... -

## 1. Introduction

In a previous work (Sieniutycz 2003 [1]) we discussed basic rules for modeling power production and energy limits in purely thermal systems with finite rates. In particular, radiation engines were analyzed. In the present work we treat generalized systems in which temperatures T and chemical potentials $\mu^k$ are essential. This is associated with engines propelled by fluxes of both energy and substance. When one, say, upper, reservoir is finite, its thermal potential decreases along the stream path, which is the consequence of the energy balance. Any finite reservoir is thus a resource reservoir. It is the resource property or the finiteness of amount or flow of a valuable substance or energy which changes the upper fluid properties along its path. Then, in the engine mode of the system, one observes fluid's

relaxation to the equilibrium with an infinite lower reservoir, usually the environment. This is a cumulative effect obtained for a resource fluid at flow, a set of sequentially arranged engines, and an infinite bath Downgrading or upgrading of resources may occur also in electrochemical systems of fuel cell type. Fuel cells working in the power production mode are electrochemical flow engines propelled by chemical reactions.

In a process of power production shown in Fig. 1 two media differing in values of T and $\mu$ interact through an energy generator (engine), and the process is propelled by diffusive and/or convective fluxes of heat and mass transferred through 'conductance' or boundary layers. The energy flux (power) is created in the generator between the resource fluid ('upper' fluid 1) and, say, an environment fluid ('lower' fluid, 2). In principle, both transfer mechanisms and values of conductance of boundary layers influence the rate of power production (Curzon and Ahlborn 1975[2]; De Vos 1994 [3], Sieniutycz and Kuran 2005 [4], 2006 [5]).

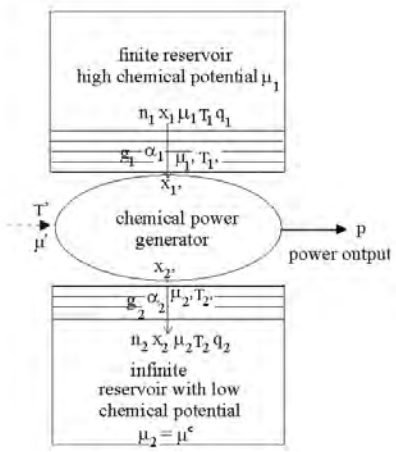


*Fig. 1. A scheme of chemical and/or thermal engine.*

## 2. Carnot Control Variables in Power Systems

Diverse controls can be applied in power systems to represent the propelling fluxes of heat and mass transfer. Here we shall recall and then use definitions of Carnot control variables (Carnot temperature and chemical potential) whose derivations and applications were originated in our previous work (Sieniutycz 2003 [8]). We begin with the simplest case of no mass transfer, i.e. we shall consider a steady, internally reversible ('endoreversible') heat engine with a perfect internal power generator characterized by temperatures of circulating fluid $T_{1'}$ and $T_{2'}$, Fig.1. The stream temperatures, attributed to the bulk o each fluid are $T_1$ and $T_2$. The inequalities $T_1 > T_{1'} > T_{2'} > T_2$ are valid for the engine mode of the system. With an effective temperature called Carnot temperature

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

entropy production of the endoreversible process, takes the following simple form

$$\sigma_s = q_1 \left( \frac{1}{T'} - \frac{1}{T_1} \right) \tag{2}$$

This form is identical with the familiar expression obtained for processes of purely dissipative heat exchange between two bodies with temperatures $T_1$ and $T'$. In terms of temperature $T'$ of Eq. (1) thermal efficiency assumes the classical Carnot form containing the temperature in the bulk of the second reservoir and temperature $T'$:

$$\eta = 1 - \frac{T_2}{T'} \tag{3}$$

This property substantiates the name "Carnot temperature" for control variable $T'$. In terms of $T'$ description of thermal endoreversible cycles is broken down to formally "classical" equations which contain $T'$ in place of $T_1$. In irreversible situations Carnot temperature $T'$ efficiently represents temperature of the upper reservoir, $T_1$. Yet, at the reversible Carnot point, where $T_{1'} = T_1$ and $T_{2'} = T_2$, Eq. (1) yields $T' = T_1$, thus returning to the classical reversible theory. These properties of Carnot temperature render descriptions of endoreversible and reversible cycles similar. They also make the variable $T'$ a suitable control in both static and dynamic cases (Sieniutycz 2003 [8]).The notion of Carnot temperature can be extended to chemical systems, where also the Carnot chemical potential emerges (Sieniutycz 2003 [8]), where instead of pure heat flux $q$ the so called total heat flux (mass transfer involving heat flux) $Q$ is introduced. The heat flux equals the difference between total energy flux $\varepsilon$ and flux of enthalpies of transferred components, $q = \varepsilon - h$, satisfying an equation

$$Q \equiv \varepsilon - \mu_1 n_1 ... \mu_k n_k ... - \mu_m n_m . \equiv \varepsilon - G \tag{4}$$

where $G$ is the flux of Gibbs thermodynamic function (Gibbs flux). The equality $\varepsilon = Q + G$ is fundamental in the theory of chemical engines; it indicates that power can be generated by two propelling fluxes: heat flux $Q$ and Gibbs flux $G$, each generation having its own efficiency. The related driving forces are the temperature difference and chemical affinity. Assuming a complete conversion we restrict to power yield by a simple reaction $A_1 + A_2 = 0$ (isomerisation or phase change of $A_1$ into $A_2$). We have a chemical control variable

$$\mu' = \mu_2 + \mu_{1'} - \mu_{2'} \tag{5}$$

which has been used earlier to study an isothermal engine (Sieniutycz 2008 [9]). After introducing the Carnot temperature in accordance with Eq. (1), total entropy production of the endoreversible power generation by the simple reaction $A_1 + A_2 = 0$ takes the following form

$$\sigma_s = Q_1 \left( \frac{1}{T'} - \frac{1}{T_1} \right) + n_1 \frac{\mu_1 - \mu'}{T'} \tag{6}$$

where $Q_1 = q_1 + T_1 s_1 n_1$ is the total heat flux propelling the power generation in the system. The resulting equation is formally equivalent with a formula obtained for the purely dissipative exchange of energy and matter between two bodies with temperatures $T_1$ and $T'$ and chemical potentials $\mu_1$ and $\mu'$.

## 3. Energy Systems with Internal Imperfections

Carnot variables $T'$ and $\mu'$ are two free, independent control variables applied in power maximization of steady and dynamical generators. Ideas referring to endoreversible systems may be generalized to those with internal dissipation. In such cases a single irreversible unit can be characterized by two loops shown in Fig. 2 which presents the temperature–entropy

diagram of an arbitrary irreversible stage. Each stage can work either in the heat-pump mode (larger, external loop in Fig. 2) or in the engine mode (smaller, internal loop in Fig. 2).

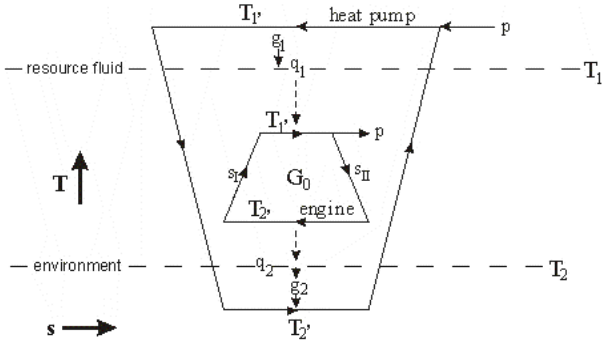


*Fig. 2. Two basic modes with internal and external dissipation: power yield in an engine and power consumption in a heat pump. Primed temperatures characterize the circulating fluid.*

The related analysis follows the earlier analyses of the problem which take into account internal irreversibility by applying the factor of internal irreversibility, $\Phi$. By definition, $\Phi = \Delta S_{2'}/\Delta S_{1'}$ (where $\Delta S_{1'}$ and $\Delta S_{2'}$ are respectively the entropy changes of the circulating fluid along the two isotherms $T_{1'}$ and $T_{2'}$ in Fig. 2) equals the ratio of the entropy fluxes across the thermal machine, $\Phi = J_{s2'}/ J_{s1'}$. Due to the second law inequality at the steady state the following inequalities are valid: $J_{s2'}/J_{s1} > 1$ for engines and $J_{s2'}/J_{s1} < 1$ for heat pumps; thus the considered ratio $\Phi$ measures the internal irreversibility. In fact, $\Phi$ is a synthetic measure of the machine's imperfection. $\Phi$ satisfies inequality $\Phi > 1$ for engine mode and $\Phi < 1$ for heat pump mode of the system. A typical goal is to derive efficiency, entropy production and power limits in terms of $\Phi$.

### *3.1. Power yield and entropy production in systems with internal imperfections*

The thermal efficiency component of any endoreversible thermal or chemical engine can always by written in the form $\eta = 1 - Q_2/Q_1$. After defining the coefficient $\Phi = 1 + T_{1'}\sigma_S^{int}/Q_1$ called the internal irreversibility factor the internal entropy balance takes the form usually applied for thermal machines

$$\Phi \frac{Q_1}{T_{1'}} = \frac{Q_2}{T_{2'}} \qquad (7)$$

One can evaluate $\Phi$ from averaged value of the internal entropy production that describes the effect of irreversible processes within the thermal machine. Clearly, in many cases $\Phi$ is a complicated function of the machine's operating variables. In those complex cases one applies the data of $\sigma_s^{int} = dS_\sigma^{int}/dt$ to calculate averaged values of the coefficient $\Phi$. In our analysis the quantity $\Phi$ is treated as the process constant. This corresponds with the observation that it is an average value of $\Phi$, evaluated within the boundaries of operative parameters of interest which is used in most of analyses of thermal machines. In terms of the Carnot temperature $T$' and factor $\Phi$ the efficiency $\eta$ , Eq. (7), assumes the simple, pseudo-Carnot form which is quite useful and general enough to describe thermal, radiative and chemical engines:

$$\eta = 1 - \Phi \frac{T_2}{T'} \qquad (8)$$

A particularly interesting role of the above formulas is observed for radiation engines which are energy systems driven by black radiation. In these systems Gibbs flux $G = 0$, whereas total heat flux $Q$ is identical with the energy flux $\varepsilon$, i.e. $Q = \varepsilon$. The majority of research papers on power limits published to date deals with systems in which there are two infinite reservoirs. To this case refer steady-state analyses of the Chambadal-Novikov-Curzon-Ahlborn engine (CNCA engine) in which energy exchange is described by Newtonian law of cooling, Curzon and Ahlborn 1975 [2], or of the Stefan-Boltzmann engine, a system with the radiation fluids and energy exchange governed by the Stefan-Boltzmann law (De Vos 1994 [3]). In a CNCA engine the maximum power point may be related to the optimum value of a free (unconstrained) control variable which may be efficiency $\eta$, heat flux $q_1$, or Carnot temperature $T'$. When internal irreversibility within the power generator play a role, the pseudo-Carnot formula (8) applies in place of Eq. (3), where $\Phi$ is the internal irreversibility factor (Sieniutycz and Kuran 2006 [5]). In terms of bulk temperatures $T_1$, $T_2$ and $\Phi$ one finds at the maximum power point

$$T'_{opt} = \left(T_1 \Phi T_2\right)^{1/2} \qquad (9)$$

For the Stefan-Boltzmann engine exact expression for the optimal point cannot be determined analytically, yet, this temperature can be found graphically from the chart $p = f(T')$. A pseudo-Newtonian model, Sieniutycz and Kuran 2006 [5], Kuran 2006 [6], which treats the state dependent energy exchange with coefficient $\alpha(T^3)$, omits to a considerable extent analytical difficulties associated with the use of the Stefan-Boltzmann equation.

## 4. Dynamical Energy Yield

### *4.1. General Issues*

When resources are finite and/or the propelling fluid flows at a finite rate, the Carnot and resource temperatures decrease along the process path. The previous (steady) analysis is replaced by a dynamic one, and the mathematical formalism is transferred from the realm of functions to the realm of functionals. Here the optimization task is to find an optimal profile of the Carnot temperature $T'$ along the resource fluid path that assures an extremum of the work consumed or delivered and – simultaneously – the minimum of the integral entropy production. Dynamical energy yield requires the knowledge of an extremal curve rather than an extremum point. This leads us to variational methods (to handle extrema of functionals) in place of static optimization methods (to handle extrema of functions). For example, the use of a pseudo-Newtonian model to quantify the dynamic power yield from radiation, gives rise to a non-exponential optimal curve describing the radiation relaxation to the equilibrium. The non-exponential shape of the relaxation curve is the consequence of nonlinear properties of the radiation fluid. Non-exponential are also other curves describing the radiation relaxation, e.g. those following from exact models involving the Stefan-Boltzmann equation (Kuran 2006 [6], Sieniutycz and Kuran 2005 [4], 2006 [5]). Optimal (e.g. power-maximizing) state $T(t)$ is accompanied by optimal control $T'(t)$; they both are components of the dynamic optimization solution.

Energy limits of dynamical processes are inherently connected with exergies, the classical exergy and its rate-dependent extensions. To obtain the classical exergy from work functionals it suffices to assume that the thermal efficiency of the system is identical with the

Carnot efficiency. On the other hand, non-Carnot efficiencies, influenced by rates, lead to 'generalized exergies'. The benefit from generalized exergies is that they define stronger energy limits than those predicted by classical exergies (Berry *at al* 2000 [7]).

### *4.2. Radiation Systems*

Radiation engines are thermal machines driven by the radiation fluid, a medium exhibiting nonlinear properties. Energy transfer rates in reservoirs containing nonlinear media can be described by various models. Usually one assumes that the energy transfer in a reservoir is proportional to the difference of absolute temperatures in certain power, $a$. The case of $a = 4$ refers to the radiation, $a = -1$ to the Onsagerian kinetics and $a = 1$ to the Fourier law of heat exchange. As the first case of the radiation engine modeling we consider a "symmetric nonlinear case" in which the energy exchange process in the energy exchange in each reservoir satisfies the Stefan-Boltzmann equation. Next we consider "hybrid nonlinear case" in which the upper-temperature fluid is still governed by the kinetics proportional to the difference of $(T^4)_i$ whereas the kinetics in the lower reservoir is Newtonian.

Here are equations of *symmetric nonlinear case*. For the "symmetric" kinetics governed by the differences in $T^a$, the Carnot representation of the total entropy production has the form

$$\sigma_s = g_1 g_2 \frac{T_1^a - T'^a}{\Phi g_1 \left(T'/T_2\right)^{a-1} + g_2} \left( \frac{(\Phi - 1)}{T'} + \left( \frac{1}{T'} - \frac{1}{T_1} \right) \right) \qquad (10)$$

Superiority of Carnot control $T'$ over the energy flux control $\varepsilon_1$ may be noted. Analytical expressions for the energy-flux representation of the entropy production or the associated mechanical power $p$ cannot generally be found in an analytical form. The work expression to be minimized is

$$W = \int_{t^i}^{t^f} \varepsilon_1 \eta dt = \int_{t^i}^{t^f} g_1 g_2 \frac{T_1^a - T'^a}{\Phi g_1 \left(T'/T_2\right)^{a-1} + g_2} \left( 1 - \Phi \frac{T_2}{T'} \right) dt \qquad (11)$$

In the case of analytical difficulties which occur for $a$ different from the unity the maximization can be performed numerically by dynamic programming using Carnot $T'$ as the free control.

We consider now *hybrid nonlinear case*. It involves the radiative heat transfer ($a = 4$) in the upper reservoir and a convective one in the lower one. To obtain an optimal path associated with the limiting production or consumption of mechanical energy the sum of the above functionals i.e. the overall entropy production

$$S_\sigma = -\int_{\tau^i}^{\tau^f} c(T_1) \left( \frac{\Phi}{\left(T_1^a + \dot{T}_1^a\right)^{\frac{1}{a}} + \dot{T}_1 \Phi g_1 / g_2} - \frac{1}{T_1} \right) \dot{T}_1 d\tau_1 \qquad (12)$$

has to be minimized for a fixed duration and defined end states of the radiation fluid. The most typical way to do accomplish the minimization is to write down and then solve the Euler-Lagrange equation of the variational problem. Analytical solution is very difficult to obtain, thus one has to rest on numerical approaches.

## 5. Finite Rate Exergies and Finite Resources

We are now in position to formulate the Hamilton Jacobi Bellman theory for systems propelled by energy flux $\varepsilon$. Two different kinds of work: first associated with the resource downgrading during its relaxation to the equilibrium and the second – with the reverse process of resource upgrading, are essential. Total power obtained from an infinite number of infinitesimal stages representing the resource relaxation is determined as the Lagrange functional.

### *5.1. Some Hamilton Jacobi Bellman Equations for Energy Systems*

We shall display some Hamilton Jacobi Bellman (HJB) equations for radiation power systems. A suitable example is a radiation engine whose power integral is approximated by a pseudo-Newtonian model of radiative energy exchange. For the *symmetric* model of radiation conversion (both reservoirs composed of radiation), where $\Phi' \equiv \Phi g_1/g_2$ and coefficient $\beta = \sigma a_v c_h^{-1}(p_m^0)^{-1}$ is related to molar constant of photons density $p_m^0$ and Stefan-Boltzmann constant σ, we obtain a HJB equation

$$\frac{\partial V}{\partial t} = \max_{T'(t)}\left\{\left(\dot{G}_c\left(1-\Phi\frac{T^e}{T'}\right)+\partial V/\partial T\right)\beta\frac{T^a - T'^a}{\left(\Phi'(T'/T_2)^{a-1}+1\right)T^{a-1}}\right\} \qquad (13)$$

For *a hybrid model* of the radiation conversion (upper reservoir composed of the radiation and lower reservoir of a Newtonian fluid the related Hamilton-Jacobi-Bellman (HJB) equation is

$$-\frac{\partial V}{\partial t^f}+\max_{T'(t)}\left\{-\left(\dot{G}_c(T)(1-\frac{\Phi T^e}{T'})+\frac{\partial V}{\partial T^f}\right)u\right\}=0 \qquad (14)$$

### *5.2. Chemical Power Systems*

The developed approach can be extended to chemical and electrochemical engines. Here we shall make only a few basic remarks. Yet, as opposed to thermal machines, in chemical ones 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 extremum power (maximum of power produced and minimum of power consumed) are static optimization problems. For a finite "upper stream", however, amount and chemical potential of an active reactant decrease in time, and considered problems are those of dynamic optimization and variational calculus. Application of chemical Carnot control $\mu'$ in terms of fuel flux $n_1$ and its mole fraction $x$ to the Lagrangian relaxation path leads to a work functional

$$W = -\int_{\tau_1^i}^{\tau_1^f}\left\{\zeta_0 + RT\ln\left(\frac{X/(1+X)+dX/d\tau_1}{x_2 - jdX/d\tau_1}\right)\right\}\frac{dX}{d\tau_1}d\tau_1 \qquad (15)$$

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

$$H(X,\dot{X}) = RT\dot{X}^2\left(\frac{1+X}{X}+\frac{j}{x_2}\right) \qquad (16)$$

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 the constancy of $H$ in Eq. (16).

## 6. Concluding Remarks

This research provides data for power production bounds (limits) which are enhanced in comparison with those predicted by the classical thermodynamics. As opposed to the classical thermodynamics, these bounds depend not only on changes of the thermodynamic state of participating resources but also on process irreversibility, ratios of stream flows, stream directions, and mechanism of heat and mass transfer. The methodology familiar for thermal machines has been extended to chemical and electrochemical engines. Extensions are also available for multicomponent, multireaction units (Sieniutycz 2009 [10]).

The generalized bounds, obtained here by solving Hamilton Jacobi Bellman equations, are stronger than those predicted by thermostatic. They do not coincide for processes of work production and work consumption; they are 'thermokinetic' rather than 'thermostatic' bounds. Only for infinitely long durations or for processes with excellent transfer (an infinite number of transfer units) the thermokinetic bounds reduce to the classical thermostatic bounds. A real process which does not apply the optimal protocol but has the same boundary states and duration as the optimal path, requires a real work supply that can only be larger than the finite-rate bound obtained by the optimization. Similarly, the real work delivered from a nonequilibrium work-producing system (with the same boundary states and duration but with a suboptimal control) can only be lower than the corresponding finite-rate bound. This is a direction with many open opportunities, especially for separation and chemical systems.

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