

Carnot Controls to Unify Traditional and Work-Assisted Operations with Heat & Mass Transfer

Stanislaw SIENIUTYCZ
Warsaw University of Technology
Faculty of Chemical and Process Engineering,
Department of Process Separation
1 Waryńskiego Street (Room 232), 00-645 Warsaw-Poland
E-mail: sieniutycz@ichip.pw.edu.pl

Abstract

This work is a synthesizing approach in which a new methodology is analyzed in the thermodynamic modelling of thermal machines and traditional heat and mass exchangers, where certain special control variables called the Carnot controls are suitable. With these controls, expressions describing the lost work and entropy production assume the same form in endoreversible thermal machines and in traditional processes of purely dissipative transport. Mathematical models of thermal machines and characteristics of endoreversible operations are particularly simple in terms of the Carnot controls. The efficiency decrease caused by the exergy dissipation and finite rate limits on mechanical energy yield or consumption are estimated in terms of maximum work released from an engine or minimum work added to a heat pump. Remarkable simplification in analysis of complex thermal machines is achieved when Carnot controls are applied. Generalized analyses include mass transfer and lead to finite time counterparts of classical available energy (exergy). For sequential-type equipment of a finite size, enhanced limits are obtained for the energy production or consumption. Progress in the theory and its applications in the energy generation problems is achieved; examples of applications are discussed.

Key words: thermodynamic optimization, efficiency, endoreversible engines, heat pumps

1. Introduction

1.1. Thermodynamic optimization

This research is a synthesizing approach that belongs in the field of thermodynamic optimization (Berry et al. 2000, Feidt 1987), a special branch of the process optimization that uses the thermodynamic performance criteria and models of constraints (Bejan et al. 1996, Sieniutycz 1991). Optimization itself is a general strategy of seeking best solutions for processes and operations in the presence of various constraints. Thermodynamic optimization uses, for example, the following performance criteria:

- a) fluxes of mechanical or electric energy,
- b) heat and work (generated or consumed),
- c) losses of mechanical energy or exergy, generation of entropy,

- d) thermodynamic state parameters at the final stage of the process (they constitute the so-called physicochemical criteria of optimization), e.g. final concentration of a valuable product in a chemical reactor.

Thermodynamic criteria are generally insufficient for economic purposes. Yet, they may sometimes be useful to assess the quality of the process economics as well. This is, for example, the case when the work flux from a thermal machine or the final concentration of the key reagent are main indicators of the profit.

1.2. Thermoeconomic optimization

A broader field is thermoeconomic optimization (Bejan et al. 1996, Sieniutycz 1991). It applies economic performance criteria formulated with the help of costs engineering and engineering economics (Bejan et al. 1996, Sieniutycz 1991). Only seldom may these economic

criteria be regarded as suitable generalizations of criteria encountered in thermodynamic optimization. Yet, thermoeconomic optimization seldom uses the same models of constraints as thermodynamic optimization especially when these constraints stem from thermodynamic balances. While formulations considered here refer to thermodynamic optimization only, possible extensions of ideas presented here to thermoeconomic optimization are not excluded. Such extensions are beyond the scope of the present paper.

1.3. Aims and scope

This paper treats thermal machines in which the role of nonequilibrium transports and optimal control theory are essential. Control rules for processes of engine type and heat-pump type are considered, both with pure heat exchange and with simultaneous heat and mass exchange. Links with exergy analyses of nonequilibrium systems and the classical problem of maximum work are essential. Illustrative examples are selected mainly from the didactic viewpoint, without an attempt to give comprehensive presentation of applications. The most important new result is the notion of the so-called Carnot control variables in terms of which the expression for the lost work in a thermal machine has the same form as in a related traditional processes of purely dissipative transport. We show that a considerable simplification in analysis of complex thermal machines (driven by mass fluxes) is achieved when these special controls are applied.

2. Basic Definitions and Ideas

2.1. Driving a multistage process by pure heat transfer

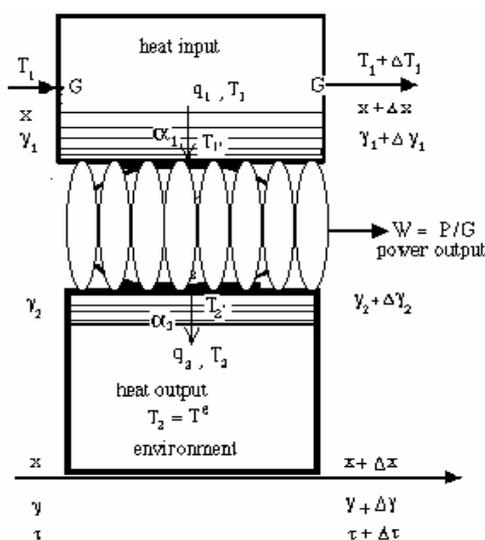


Figure 1. A multistage CACN operation as a process with active heat exchange between two fluids (in the engine mode $\Delta T_1 \leq 0$).

Consider an arbitrary one-stage process of the multistage operation of Curzon-Ahlborn-Chambadal-Novikov (CACN; Findeisen et al. 1980, Novikov 1957), Figure 1.

Our addressing of the multistage problem in Fig. 1 should be preceded by an explanation of how our work fits on the framework provided by the older work. Restricted to pure heat transfer, the problem of engine extracting the most exergy from a continuous hot stream was posed in the *reversible* limit by Bejan (1982). Whereas its endoreversible generalizations were solved a decade and half later (Sieniutycz 1997a, Sieniutycz 1999, Bejan and Errera 1998, Sieniutycz and von Spakovsky 1998), only the papers of Sieniutycz and Berry (2000), Sieniutycz (1999c) deal explicitly with cascades as genuine discrete systems with a small number of stages. The suitable mathematical structures related to the problem in Fig. 1 are difference rather than differential equations. Yet, each stage is the classical CACN process working with its own thermal parameters. Bejan and Errera's (1998) paper is restricted to the pure heat transfer as the engine propelling process, thus a general theory involving the mass diffusion that is pursued in the present paper cannot be built on its basis. On the other hand, the theory of the author's 1999 paper (Sieniutycz 1999c) does involve both heat and mass diffusion as propelling processes. Consequently, only the theory and results of Sieniutycz (1999c) constitute a sufficient basis to develop a general scheme of Carnot variables when both heat and mass fluxes are present.

The notion that the Curzon-Ahlborn-Chambadal-Novikov" idea is "well known" should be understood with care. Novikov (1957) work was unknown until Bejan discovered it in the engineering literature of the 1950s; he also discovered Chambadal (1957) and Chambadal (1963). This history is recounted in Bejan's book (Bejan 1996) and in some of his papers. In the present work, the new point is the systematic treatment of diverse irreversible operations in terms of particular quantities called the Carnot controls that were first proposed in the paper Sieniutycz (1999b). Yet that theory is restricted to the heat driven processes. This restriction is omitted in the present work.

For the purposes of the present paper it is unimportant whether its main original task - introduction and application of Carnot control variables - is illustrated with a known or an unknown example. We have chosen the operations of single-stage and multistage CACN as they are familiar to many readers, thus most of them can easily grasp the main ideals. However, the novelty of the present contribution lies on the side of methodology, not on the side of the system's

choice. Our work fits on the framework provided by the older work by synthesizing the scientific information contained in the past work of various authors in the field (including Bejan (1982), Bejan (1996), de Vos (1992), the present author (Sieniutycz 1997b) and many others, as shown in references).

The classical characteristics based on efficiency as possible control are well known, *Figure 2*.

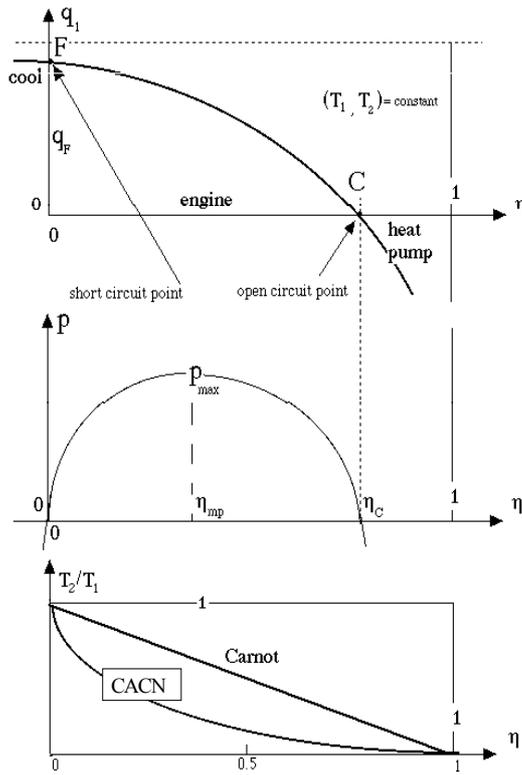


Figure 2. Conventional characteristics of a single CACN stage: the efficiency η is the control variable.

From the energy and entropy balance of the endoreversible CACN operation, a structural property of the system follows which is called here Carnot temperature T' . In our earlier work (Sieniutycz 1999b) T' was also called the driving temperature due to its specific properties. In terms of upper and lower temperatures of the circulating medium T_1 and T_2 , Carnot temperature is defined as:

$$T' = T_2 \frac{T_1}{T_2} \quad (1)$$

When the second reservoir is the environment, $T_2 = T^e$ and Eq. (1) is used in an equivalent form:

$$T' = T^e \frac{T_1}{T_2} \quad (2)$$

The primary property of T' is that in terms of T' and T_2 the thermal efficiency of the endoreversible engine is given by the Carnot formula in which T' replaces T_1 :

$$\eta = 1 - \frac{T_2}{T'} = 1 - \frac{T_2}{T_1} \quad (3)$$

A similar expression holds when the second reservoir is the environment i.e. $T_2 = T^e$:

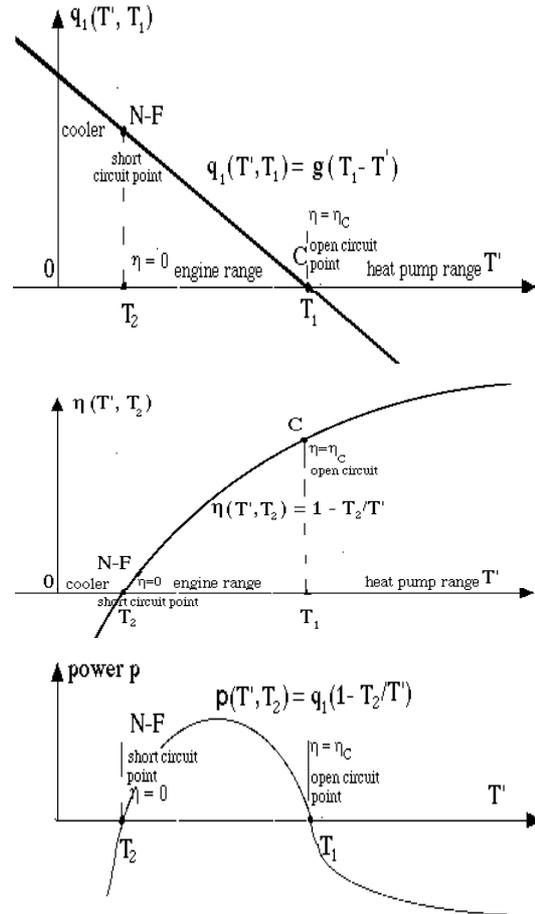


Figure 3: Characteristics of a single CACN stage when the Carnot temperature T' is the control variable.

Whenever $T_1 = T_2$ ("short circuit"), the process is purely dissipative and:

$$T' = T_2 \quad \text{or} \quad T' = T^e \quad (4)$$

Along with the efficiency formula (1), this describes an absence of mechanical energy production at the short circuit point. Otherwise at the Carnot point (open circuit point, where the process is quasistatic):

$$T' = T_1 \quad (5)$$

This means that the engine efficiency Eq. (3) now equals $\eta = \eta_c = 1 - T_2/T_1$ in accordance with the classical result of Carnot. The crucial

issue is, however, that the two forms of Eq. (3) hold for diverse irreversible processes, with various contribution of dissipation, stretching through Newton-Fourier and Carnot regions, as shown in *Figures 3 and 4*. We use the name Newton-Fourier region as in this region the heat flux satisfies Newton's cooling formula which is, in fact, the result of Fourier's law of heat conduction

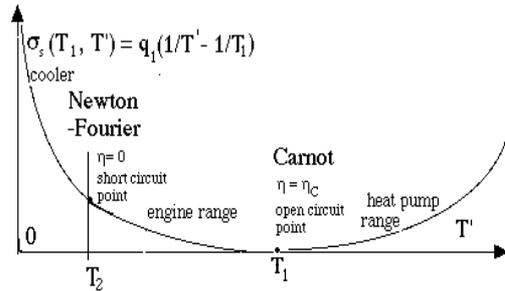


Figure 4. Entropy production in a single CACN stage when Carnot temperature T' is the control variable. In terms of Carnot variables classical thermodynamic formulae are extended to irreversible operations with work production or consumption.

2.2. Driving a single stage process by simultaneous heat and mass transfer

Consider first a power generation expression and related quantities in terms of properties of circulating fluid. After combining energy and entropy balances, the power generated or consumed in an endoreversible machine can be obtained in the form (Sieniutycz 1999c):

$$\dot{w} = \left(1 - \frac{T_2'}{T_1'}\right) q_1 + [h_1' - h_2' - T_2'(s_1' - s_2')]n \quad (6)$$

where n is the conserved mass flux. This equation refers to the (primed) heat flux representation and corresponds with a general bilinear structure of power expressions with an efficiency vector (η, β') in the equation:

$$p = \dot{w} = \eta(q_1', n)q_1' + \beta'(q_1', n)n \quad (7)$$

see, e.g., (de Vos 1992). Here the second component of power emerges which is associated with the work production (consumption) due to the mass transfer. Its interpretation is the product of mass flow n and an exergy-like function $\beta' = h_1' - h_2' - T_2'(s_1' - s_2')$ whose structure follows from a combination of the energy and (conservative) entropy balances in terms of pure heat flux. For more details, see our earlier work Sieniutycz (1999c). The endoreversible thermal efficiency (i.e. that in terms of the properties of circulating fluid) is the same as in the process of pure heat transfer

$$\eta = 1 - \frac{T_2'}{T_1'} \quad (8)$$

The thermal efficiency is the first component of the 2D efficiency vector. It is important that the thermal component of efficiency, i.e. the quantity η , remains unchanged after passing to a suitable process description that involves the total energy flux ε instead of the heat flux q . For the first fluid the quantity ε satisfies the definitive expression $\varepsilon_1 = q_1 + h_1 n_1 = q_1' + h_1' n_1 = \varepsilon_1'$. A similar expression holds for the second fluid with the index 2. The virtue of the flux ε is that the power production formula in terms of ε contains the difference of the Planck potentials that are ratios of the chemical potentials and the absolute temperature:

$$\dot{w} = \varepsilon_1 \left(1 - \frac{T_2'}{T_1'}\right) + T_2' \left(\frac{\mu_1'}{T_1'} - \frac{\mu_2'}{T_2'}\right) n_1 \quad (9)$$

This makes the introduction of Carnot chemical potentials easy. The second component of the efficiency is represented by the driving force:

$$\delta' = T_2' \left(\frac{\mu_1'}{T_1'} - \frac{\mu_2'}{T_2'}\right) \quad (10)$$

In this case the power expression is in "the energy flux representation". Still it conforms with the general bilinear structure (de Vos 1992):

$$p = \dot{w} = \eta(\varepsilon_1', n)\varepsilon_1' + \delta'(\varepsilon_1', n)n \quad (11)$$

In the original model the efficiency components (8) and (10) depend on two unknown (primed) temperatures and two unknown (primed) chemical potentials of circulating fluid, linked by a reversible entropy balance and a mass balance across the reversible part of the system. Thus these efficiencies are very difficult to use in their original form (8) and (10), and a method to overcome the difficulty should be designed. We will show that the Carnot quantities play an essential role in this matter.

We shall pass now to corresponding relationships in terms of the Carnot quantities. The definition of T' given in Sec. 2.1 applies without any changes when mass transfer accompanies heat transfer. Likewise the Carnot chemical potential, μ' , is defined, which is expressed by the parameters of circulating fluid (T_1' , T_2' , μ_1' and μ_2') as follows:

$$\mu' = T' \left(\frac{\mu_2'}{T_2'} + \left(\frac{T_2'}{T_1'}\right) \left(\frac{\mu_1'}{T_1'} - \frac{\mu_2'}{T_2'}\right)\right) \quad (12)$$

When the second reservoir is the environment, the quantities subscripted with the index 2 are replaced by those superscripted by the index

e (the environment). In any process with mass transfer, the work production is characterized by the vector of thermal efficiencies (η, δ'), such that its first component has the Carnot structure of efficiency (3).

We shall display now the corresponding relationships in terms of Carnot quantities. The thermodynamic functions of state associated with Carnot temperatures and chemical potentials are called Carnot functions. In this way we may deal with Carnot energy, enthalpy, entropy, etc. For an irreversible engine process, under the endoreversibility assumption, we obtain in terms of the Carnot intensive parameters of the fluid 1:

$$\eta = 1 - \frac{T_2}{T'} = 1 - \frac{T^e}{T'} \quad (13)$$

and

$$\delta' = T_2 \left(\frac{\mu'}{T'} - \frac{\mu_2}{T_2} \right) \quad (14)$$

Eq. (14) can also be given in terms of the reservoir's parameters. Thus in terms of Carnot thermodynamic properties, the *reversible* structure of basic equations is preserved in irreversible cases, and prediction is possible of irreversible process equations on the basis of well-known or easily-derived equations of reversible processes.

At the short circuit point the equalities $T' = T_2$ and $\mu' = \mu_2$ (or $T' = T^e$ and $\mu' = \mu^e$) hold and all components of the efficiency vector (η, δ') vanish. On the other hand, at the Carnot point the efficiencies refer to the quasistatic process. In this case, the efficiency vector has the “reversible” components:

$$\eta = 1 - \frac{T_2}{T_1} \quad (15)$$

and

$$\delta = T_2 \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) \quad (16)$$

Leaving aside the above special cases and returning to the general problem, we can state that a general optimization task is to seek optimal T' and μ' which maximize power p in “Carnot variables representation”:

$$p \equiv \dot{w} = \eta(T', T_2) \varepsilon_1(T', T_1, \mu', \mu_1) + \delta'(T', T_2, \mu', \mu_2) n(T', T_1, \mu', \mu_1) \quad (17)$$

Here the Carnot temperature and chemical potentials are independent variables and the power extremizing is with respect to these Carnot variables. The reversible balances of entropy

and mass across the reversible thermal machine are already included; thus the extremizing procedure works without constraints. In an alternative case, all working quantities may be expressed in terms of the fluxes in the system, of energy ε_1 and of mass n_1 . A procedure working with heat flux q (which is omitted here) can also be designed. See some examples in the next section. In this case the extremizing takes place with respect to the fluxes q_1 and n_1 .

In the simplest case of pure linear heat transfer:

$$\varepsilon_1 = q_1(T', T_1, \mu', \mu_1) = g(T_1 - T') \quad (18)$$

where g is the overall conductance of heat transfer satisfying $1/g = 1/g_1 + 1/g_2$. This was, in fact, shown by elementary calculations in many works, see, e.g., refs. Sieniutycz (1999b) and de Vos (1992). It follows from Eq. (17) that at the Carnot point, where $T' = T_1$, the reversible heat flux equals zero, which means the quasistaticity property. On the other hand, at the short circuit point, where $T' = T^e$, the usual Newton-Fourier formula describes the heat flow which drives the thermal engine.

When the mass transfer is coupled with the heat transfer, an exact approach requires using Onsager's theory to evaluate the fluxes ε_1 and n_1 in terms of differences of temperature reciprocals and the ratios of chemical potentials and T . Whenever working with fluxes other than (ε, n), the introduction of a suitable Carnot-like chemical potential may or may not be possible. Arguing from a general standpoint this also refers to Carnot temperature T' . Apparently T' emerges as a quantity independent of transformation of thermodynamic fluxes, at least if one is restricted to fluxes common in irreversible thermodynamics. In general, however, various definitions of T' or μ' may or may not be possible in various coordinate systems. This means that neither T' nor μ' can be introduced on a purely formal basis, i.e. without reference to a specific coordinate system. Yet, suitable approximations are allowed in equations with T' or μ' . The heat flux q_1 can be evaluated as proportional to the difference in temperatures (or in temperature reciprocals for a suitably modified heat conductance), as in Eq. (18). Mass flux can be expressed as proportional to the difference in concentrations of the active component (Sieniutycz 1999c). In agreement with the Lewis analogy:

$$n(T', T_1, \mu', \mu_1) = g c^{-1} (X_1 - X') \quad (19)$$

Here c is the specific heat of the fluid and $g c^{-1}$ is the overall mass transfer conductance.

2.3. Finite resources and work optimization in dynamical problems

We shall now pass to sequential processes. This case, which is derived from the multistage systems theory, involves differentials and work functionals. It is assumed that the second fluid constitutes an infinite constant reservoir whereas the first fluid changes its properties when it proceeds through stages in time. Enthalpy changes are attributed to the total energy flux ε . In the formulae below we use the symbol T for the variable temperature $T_1(t)$. For an endoreversible flow process, the specific work obtained in terms of the Carnot controls is:

$$\begin{aligned} W \equiv P/G &= - \int_{T_i}^{T_f} \left\{ \left(1 - \frac{T^e}{T}\right) dH + T^e (\mu'/T' - \mu^e/T^e) dX \right\} \\ &= - \int_{T_i}^{T_f} \left\{ \left(1 - \frac{T^e}{T}\right) dH + T^e (\mu/T - \mu^e/T^e) dX \right\} \\ &\quad - T^e \int_{T_i}^{T_f} \left\{ (1/T - 1/T') dH + (\mu'/T' - \mu/T) dX \right\} \end{aligned} \quad (20)$$

The expression in the first integral was split into the reversible or path-independent part which is independent on Carnot controls (the second integral) and an irreversible or path-dependent part which depends on these controls (the third integral). The result (20) leads to a generalized or finite time exergy $A = \max W$ satisfying the formula:

$$\begin{aligned} A = \max W &\equiv \max P/G \\ &= \max_{T_i} \int_{T_i}^{T_f} \left\{ - \left(1 - \frac{T^e}{T}\right) dH - T^e (\mu'/T' - \mu^e/T^e) dX \right\} \\ &= H^i - H^f - T^e (S^i - S^f) - \mu^e (X^i - X^f) \\ &\quad - T^e \min_{T_i} \int_{T_i}^{T_f} \left\{ (1/T - 1/T') dH + (\mu'/T' - \mu/T) dX \right\} \end{aligned} \quad (21)$$

Consequently the (maximum) work produced by the engine is equal to the change of the classical exergy reduced by the product of the reservoir's temperature and the (minimum) entropy production.

An analogous equation is obtained for the heat pump, but then the effect of entropy production is added to the classical exergy change, i.e. an increase of the work input is necessary to assure the required state change in a finite time. Eq. (21) expresses - in terms of Carnot controls - the Gouy-Stodola law for the endoreversible system (Bejan 1982, Sieniutycz 1997b). The thermodynamic form of the entropy source (without kinetics incorporated) is classical in terms of the Carnot controls, and it is the sum of products of thermodynamic fluxes and forces:

$$S_\sigma = \int_{T_i}^{T_f} \left\{ (1/T - 1/T') \dot{H} + (\mu'/T' - \mu/T) \dot{X} \right\} d\tau \quad (22)$$

The kinetic form of this source, which incorporates Onsager's relations, is classical as well, i.e. it is the same as in processes without production or consumption of mechanical energy:

$$\begin{aligned} S_\sigma &= \int_{T_i}^{T_f} \left\{ r^{HH} \dot{H}^2 + 2r^{HX} \dot{H} \dot{X} + r^{XX} \dot{X}^2 \right\} d\tau \\ &= \int_{T_i}^{T_f} \left\{ g^{HH} (1/T - 1/T')^2 + 2g^{HX} (1/T_2 - 1/T') \right. \\ &\quad \left. (\mu'/T' - \mu/T) + g^{XX} (\mu'/T' - \mu/T)^2 \right\} d\tau \end{aligned} \quad (22)$$

This classical structure implies the constancy of rates and forces along an optimal path, and also the constancy of the entropy production (the so-called "equipartition of the entropy production", first systematically treated by Tondeur and Kvaalen 1887). Yet this property holds only for linear processes in which conductance coefficients are state-independent constants and no constraints are imposed on control variables. Examples are the Fourier heat exchange, linear mass diffusion, first-order chemical reactions, etc.

3. Examples of Carnot Temperatures in Spaces of Flows

In spaces of flows or time derivatives of state variables (rates) Carnot variables are some operator expressions which depend on process state and flow or time derivative characterizing the process. Expressions given below show respective formulae for processes recently treated in the literature. We restrict to the Carnot temperature operator T' and related thermal efficiencies.

3.1. Classical CACN process with Newton's heat exchange

When Fourier-Newton heat exchange takes place on both parts of the engine and the partial conductances are g_1 and g_2 , then the Carnot temperature:

$$T' \equiv T_1 - q_1 / g \quad (23)$$

where q_1 is the driving heat flux (on the high- T part of the engine) and g is the overall conductance which results as the reciprocity of the sum of the partial heat resistances, $g = (1/g_1 + 1/g_2)^{-1}$ or $g_1 g_2 / (g_1 + g_2)$. The resulting thermal efficiency satisfies the well-known formula (de Vos 1992):

$$\eta \equiv 1 - \frac{T_2}{T'} = 1 - \frac{T_2}{T - q_1 / g} \quad (24)$$

3.2. Non-Newtonian heat exchange with power exponent α

Here we deal with the case when the heat exchange on the side of the high-T fluid is non-Newtonian and that on the side of the low-T fluid is Newtonian. The respective formula for T' is:

$$T' = T_1 - (q_1/g_1)^{1/\alpha} - q_2/g_2 \quad (25)$$

Sieniutycz (2000) hence the efficiency:

$$\eta = 1 - \frac{T_2}{T'} = 1 - \frac{T_2}{T_1 - (q_1/g_1)^{1/\alpha} - q_2/g_2} \quad (26)$$

Of course in these cases heat flux q_1 is identical with energy flux ε .

3.3. Simultaneous heat and mass transfer

The Carnot temperature evaluated from the results of (Sieniutycz 1999c) is:

$$T'(q_1, n) = \left(\frac{c_1 g_{m1}}{c_1 g_{m1} - c_1 n} \right) \frac{q_1}{g} \left(\frac{(1 + X_1)^{(1+X_1)}}{(X_1)^{(X_1)}} \right)^{(R g_{m1}/c_2 g_{m2})} \cdot \left(\frac{(X_1 - n/g_{m1})^{(X_1 - n/g_{m1})}}{(1 + X_1 - n/g_{m1})^{(1+X_1 - n/g_{m1})}} \right)^{(R g_{m1}/c_2 g_{m2})} \cdot \left(\frac{(1 + X_2)^{(1+X_2)}}{(X_2)^{(X_2)}} \right)^{(-R g_{m2}/c_2 g_{m2})} \cdot \left(\frac{(X_2 + n/g_{m2})^{(X_2 + n/g_{m2})}}{(1 + X_2 + n/g_{m2})^{(1+X_2 + n/g_{m2})}} \right)^{(-R g_{m2}/c_2 g_{m2})} \quad (27)$$

where the partial conductances indexed by m refer to mass transfer. This result is in terms of the pure heat flux q_1 rather than the energy flux ε . R is the gas constant, c_1 and c_2 are the specific heats of the first and second fluid, g_{m1} and g_{m2} are related conductances of mass transfer, and X_1 and X_2 are concentrations of the active component. Again, the thermal efficiency is calculated as $\eta = 1 - T_2/T'$. Both results can contribute to the present theory of active drying processes (Sieniutycz 1999d).

4. Non-Typical Use of Carnot Variables

Taking into account the power and simplicity of models that use Carnot variables, a basic question can be asked about physical and mathematical conditions that constraint definition and effective use of Carnot controls T' and μ' . The following test answers this question.

4.1. Application to endoreversible radiative engine

We consider the so-called Stefan-Boltzmann engine (de Vos 1992), where both heat exchanges satisfy the radiation laws:

$$q_1 = g_1(T_1^4 - T_1'^4), \quad q_2 = g_2(T_2^4 - T_2'^4) \quad (28)$$

The continuity condition for the entropy flux across an endoreversible radiative engine has the form:

$$g_1(T_1^4 - T_1'^4)/T_1' = g_2(T_2^4 - T_2'^4)/T_2' \quad (29)$$

The substitution of Eq. (29) of the second primed temperature in the form $T_2' = T_1' T_2 / T_1'$ leads to the temperatures of the circulating fluids in terms of T_1, T_2 and:

$$(T_1')^4 = \frac{g_1}{g_1 + g_2(T_2/T_1')^3} (T_1)^4 + \frac{g_2}{[g_1 + g_2(T_2/T_1')^3](T_2/T_1')^3} (T_2)^4 \quad (30)$$

$$(T_2')^4 = \frac{g_1}{g_1 + g_2(T_2/T_1')^3} (T_2/T_1')^4 (T_1)^4 + \frac{g_2}{[g_1 + g_2(T_2/T_1')^3]} (T_2/T_1')^3 (T_2)^4 \quad (31)$$

The use of Eq. (30) in the first formula of Eq. (28) yields:

$$q_1 = g_1 g_2 \frac{T_1^4 - T_1'^4}{g_1(T_1'/T_2)^3 + g_2} \quad (32)$$

Similarly an equation for q_2 is obtained. For this purpose the equality $T'' = T_1 T_2$ can also be used. The heat q_2 equals $q_1(1 - \eta) = q_1 T_2 / T_1'$, whence, in terms of the second Carnot control T'' :

$$q_2 = g_1 g_2 \frac{T_1'^4 - T_2^4}{g_1 + g_2(T_1''/T_1)^3} \quad (33)$$

At the Carnot point:

$$T' = T_1 = T_1', \quad T'' = T_2 = T_2', \quad \eta = 1 - T_2/T_1, \quad q_1 = q_2 = p = 0.$$

In conclusion, heat fluxes expressed in terms of their own Carnot controls (T' for q_1 and T'' for q_2) satisfy equations that are similar but not identical with equations of a related process without work. This is caused by the nonlinearity of the transfer process in the case of radiation. Only at the short circuit point, where $T' = T_2$ and $T'' = T_1$ along with $q_1 = q_2$, Eqs. (32) and (33) yield the kinetics known from traditional processes:

$$q_1 = g[T_1^4 - T_1'^4] = g[T_1''^4 - T_2^4] \quad (34)$$

5. Concluding Remarks

It follows from the analysis of the radiation engine that the overall kinetics expressed in

terms of the temperatures T' or T'' is identical in operations with and without work only when involved transport processes are linear. In nonlinear cases, the overall kinetics differ in both kinds of operations. Yet, the benefits that result from describing thermal machines in terms of Carnot variables are preserved in all thermodynamic relations. They follow from a common expression for the maximum work potential (or the entropy source), the same for operations with and without work. For processes without chemical reactions and those large numbers of transports in which linear approximations are acceptable, the models and optimization results in both kinds of operations are identical. This offers a good opportunity to predict optimal controls and optimal trajectories for difficult processes in thermal machines with coupled heat and mass transfer by applying the well-elaborated optimization results obtained for classical heat and mass exchangers. Future research will include complex chemical processes with nonlinear resistances (Grabert et al. 1983, Shiner 1987).

Acknowledgments

The author acknowledges the financial support from a Warsaw TU grant *Dynamics of Complex Systems* in the academic year 2002/2003. Referees' remarks were very helpful to discover inconsistencies in the original manuscript.

Nomenclature

A	generalized exergy
A	exchange area
c	specific heat
G	fluid flow
g	overall conductance
g_1, g_2	partial conductances
H	enthalpy of controlled phase
n	molar mass flux
P, p	total and local power
q_1'	heat flux at state 1' (Fig. 1)
r	overall resistance
S	entropy
T	absolute temperature
S_σ	entropy production
t	physical time
W	specific work
X	concentration of active component
α	heat exchange coefficient
β'	material efficiency in the frame with heat flux
γ	cumulative conductance
δ	material efficiency in the frame with energy flux
ε	energy flux
η	thermal efficiency
μ	chemical potential
τ	nondimensional time

References

- Bejan, A., 1982, *Entropy Generation Through Heat and Fluid Flow*, p. 18., Wiley, New York.
- Bejan, A., 1996, *Entropy Generation Minimization*, CRC Press, Boca Raton, FL.
- Bejan, A., Errera, M. R., 1998, "Maximum power from a hot stream", *Int. J. Heat Mass Transfer*, Vol. 41, 1998, pp. 2025-2036.
- Bejan, A., Tsatsaronis, G., Moran, M., 1996, *Thermal Design and Optimization*, Wiley, New York.
- Berry, R. S., Kazakov, V. A., Sieniutycz, S., Szwasz, Z., Tsirlin, A. M., 2000, *Thermodynamic Optimization of Finite Time Processes*, Wiley, Chichester, ISBN 0471-96-7521.
- Chambadal, P., 1957, *Les Centrales Nucleaires*, Armand Colin, Paris.
- Chambadal, P., 1963, *Evolution et Applications du Concept d'Entropie*, Dunod, Paris.
- Curzon, F. L., Ahlborn, B., 1975, "Efficiency of Carnot engine at maximum power output, Amer." *J. Phys.* 43, 22-24.
- Feidt, M., 1987, *Thermodynamique et optimisation énergétique des systemes et procédés*, Paris, Lavoisier, (second ed. in 1996).
- Findeisen, W., Szymanowski, J., Wierzbicki, A., 1980, "Teoria i Metody Obliczeniowe Optymalizacji, Panstw. Wydawnictwa Naukowe, Warszawa", ISBN 83-01-00976-4.
- Grabert, H., Hänggi, P., Oppenheim, I., 1983, "Fluctuations in reversible chemical reactions". *Physica* 117A 300-316.
- Novikov, I. I., 1957, "The efficiency of atomic power stations", *Atomnaya Energiya* 3, 409, English translation in *J. Nuclear Energy II*, 7 (1958), 125.
- Shiner, J. S., 1987, "Algebraic symmetry in chemical reaction systems at stationary states arbitrarily far from thermodynamic equilibrium", *J. Chem. Phys.* 87 1089-1094 ().
- Sieniutycz, S., 1991, *Optymalizacja w Inzynierii Procesowej*, WNT, Warszawa, ISBN 83-204-1074-6
- Sieniutycz, S., 1997a, "Generalized Carnot problem of maximum work in finite time via Hamilton-Jacobi-Bellman equation", *Proceedings of FLOWERS 97* (Florence World Energy Research Symposium, 30 July-1 August 1997), SGE, Padova 1997, pp. 151-159. ISBN 88-86281-21-8.
- Sieniutycz, S., 1997b, "Hamilton-Jacobi-Bellman Theory of Dissipative Thermal Availability", *Phys. Rev. E* 56, 5051-5064 (1997).

Sieniutycz, S., 1997c, "Irreversible Carnot problem of maximum work via Hamilton-Jacobi-Bellman theory", *J. Nonequilib. Thermodyn.* 22, 260-284, ISSN 0340-0204 (1997).

Sieniutycz, S., 1999a, "Carnot problem of maximum work from a finite resource interacting with environment in a finite time", *Physica A* 264, 234-263 (1999).

Sieniutycz, S., 1999b, "Endoreversible modelling and optimization of thermal machines by dynamic programming", Chap. 11 in: *Advance in Recent Finite Time Thermodynamics*, pp. 189-220, ed. Ch. Wu, Nova Science, New York, ISBN 1-56072-644-4 (1999).

Sieniutycz, S., 1999c, "Optimal control framework for multistage endoreversible engines with heat and mass transfer", *J. of Non-Equilibrium Thermodynamics*, 24, 40-74, ISSN 0340-0204 (1999).

Sieniutycz, S., 1999d, "Thermodynamic optimization for work-assisted heating and drying operations", *Energy & Conversion Management*, 41, 2009-2039, ISSN 0196-8904 (1999).

Sieniutycz, S., 2000, "Work optimization in continuous and discrete systems with complex fluids", *Journal of Non-Newtonian Fluid Mechanics*, 96, 341-370, (2000).

Sieniutycz, S., Berry, R. S., 2000, "Discrete Hamiltonian Analysis of Endoreversible Thermal Cascades", Chapter 6 in the book: *Thermodynamics of Energy Conversion and Transport*, eds. S. Sieniutycz and A. de Vos, Springer N.Y., 2000, pp. 143-172. ISBN 0-387-98938-2.

Sieniutycz, S., von Spakovsky, M., 1998, "Finite Time Extension of Thermal Exergy", *Energy & Conversion Management*, 39 (No. 14), 1423-1447.

Tondeur, D. and Kvaalen, E., 1887, "Equipartition of entropy production: an optimality criterion for transfer and separation processes", *Ind. Eng. Chem. Research* 26, 50-56.

de Vos, A., 1992, *Endoreversible Thermodynamics of Solar Energy Conversion*, pp. 29-51, Clarendon Press, Oxford, ISBN 019851 3925.