

CODEN STJSAO  
ZX470/1599ISSN 0562-1887  
UDK 532.51:621.353.5:519.61

# Thermodynamic Basis of Thermo-Chemical Energy Systems and Fuel Cells\*

*Stanislaw SIENIUTYCZ*

Faculty of Chemical & Process Engineering,  
Warsaw University of Technology,  
1 Waryńskiego Street, Warsaw,  
Poland

sieniutycz@ichip.pw.edu.pl

## Keywords

Power generators  
Chemical reactions  
Efficiency  
Fuel cells  
Power limits

## Ključne riječi

Generatori električne energije  
Kemijske reakcije  
Učinkovitost  
Gorivni članci  
Granice snage

**Primljeno (Received):** 2011-12-12  
**Prihvaćeno (Accepted):** 2012-05-30

## 1. Introduction

This paper reviews a synthesizing thermodynamic approach to modeling and power optimization in diverse energy converters, such as thermal, solar and chemical engines. Thermodynamic principles lead to a converter's efficiency and limiting generated power. Efficiency equations serve to solve problems in the upgrading and downgrading of a resource medium. Real work yield is a cumulative effect obtained in a system of a resource fluid, engines, and an infinite bath. While optimization of steady systems requires the use of differential calculus and Lagrange multipliers, dynamic

*Original scientific paper*

Abstract: This research treats power optimization for energy converters, such as thermal, solar and electrochemical engines (fuel cells). A common methodology is developed for the assessment of power limits in thermal systems and fuel cells. Thermodynamic analyses lead to converter efficiency and limiting power. Steady and dynamic systems are investigated. Static optimization of steady systems applies the differential calculus or Lagrange multipliers, dynamic optimization of unsteady systems uses variational calculus and dynamic programming. The primary result of the first is the limiting value of power, whereas that of the second is a total generalized work potential. The generalizing quantity depends on the thermal coordinates and a dissipation index,  $h$ , i.e. the Hamiltonian of the problem of minimum entropy production. The advanced thermodynamics, of an irreversible nature, implies stronger bounds on work delivered or supplied than the classical reversible work. It is shown how various analytical developments can efficiently be synthesized to quantitatively evaluate power limits in thermal systems and fuel cells of a simple topology (without countercurrent flows).

## Termodinamičke osnove termokemijskih energetske sustava i gorivnih članaka\*

*Izvorno znanstveni članak*

Sažetak: Ovo se istraživanje bavi optimizacijom snage sustava za pretvorbu energije poput termičkih, solarnih i elektrokemijskih (gorivni članci). U radu je razvijena jedinstvena metoda procjene granice snage u termičkim sustavima i gorivnim člancima. Termodinamičkim analizama dolazi se do učinkovitosti sustava za pretvorbu i granične snage. Istražuju se stacionarni i nestacionarni sustavi. Za statičku optimizaciju stacionarnih sustava primjenjuju se diferencijalni račun ili Lagrangeovi faktori; dinamička optimizacija nestacionarnih sustava koristi varijacijski račun i dinamičko programiranje. Rezultat prvog je ograničavajuća vrijednost snage dok je rezultat drugog ukupni poopćeni potencijal rada. Poopćenje ovisi o termičkim koordinatama i indeksu disipacije,  $h$ , npr. Hamiltonov operator problema minimalne entropije. Razvijena termodinamika nepovratnih sustava implicira čvršće granice na potrošeni ili predani rad nego što je to kod termodinamike povratnih procesa. Pokazano je kako različite analize mogu efikasno biti sintetizirane u svrhu kvantitativne procjene granice snage u termičkim sustavima i gorivnim člancima jednostavne topologije (bez protustrujnih tokova).

optimization involves variational calculus and dynamic programming. The primary result of the static optimization is the limiting value of power, whereas that of the dynamic optimization (treated here with particular care) is a finite-rate counterpart of the classical potential of reversible work (exergy). This generalized potential depends on thermal coordinates and a dissipation index,  $h$ , i.e. the Hamiltonian of the related problem of minimum entropy production. The generalized potential implies stronger bounds on work delivered or supplied than the reversible work potential. In reacting systems the chemical affinity constitutes a

prevailing counterpart of the thermal efficiency. Therefore, in reacting mixtures flux balances are applied to derive power yield in terms of an active part of chemical affinity. The power maximization approach is finally applied for fuel cells treated as flow engines driven by fluxes of chemical reagents and the electrochemical mechanism of electric current generation. Analyzed are the performance curves of a SOFC system and the effect of typical design and operating parameters on the cell performance. The theory combines a recent formalism worked out for chemical machines with the Faraday's law which determines the intensity of the electric current generation. The steady-state model of a high-temperature SOFC is considered, which refers to constant chemical potentials of incoming hydrogen fuel and oxidant. Lowering of the cell voltage below its reversible value is attributed to polarizations and

imperfect conversions of reactions. A power formula summarizes the effect of transport laws, irreversible polarizations and the efficiency of power yield.

The reversible electrochemical theory is extended to the case with dissipative chemical reactions; this case includes systems with incomplete conversions, characterized by "reduced affinities" and an idle run voltage. The efficiency decrease is linked with thermodynamic and electrochemical irreversibilities expressed in terms of polarizations (activation, concentration and ohmic). The effect of incomplete conversions is modeled in a novel way assuming that substrates can remain after the reaction and that side reactions may occur. Optimum and feasibility conditions are obtained and discussed for some important input parameters such as the efficiency, power output, and electric current density of the cell.

### Symbols/Oznake

$a$	- temperature power exponent - temperaturna provodnost
$C$	- specific heat [ $\text{Jg}^{-1}\text{K}^{-1}$ , $\text{Jm}^{-3}\text{K}^{-1}$ , $\text{Jmol}^{-1}\text{K}^{-1}$ ] - specifični toplinski kapacitet [ $\text{Jg}^{-1}\text{K}^{-1}$ , $\text{Jm}^{-3}\text{K}^{-1}$ , $\text{Jmol}^{-1}\text{K}^{-1}$ ]
$D^n, \tilde{D}^n$	- generalized profit and gauge profit at stage $n$ - poopćena dobit i dobit razlike na stupnju $n$
$G$	- Gibbs function - Gibbs-ova funkcija
$\dot{G}$	- resource flux [ $\text{gs}^{-1}$ , $\text{mols}^{-1}$ ] - tok izvora [ $\text{gs}^{-1}$ , $\text{mols}^{-1}$ ]
$f$	- rate vector with components $f_1, \dots, f_k, \dots, f_s$ - vektor brzine s komponentama $f_1, \dots, f_k, \dots, f_s$
$f_0$	- intensity of generalized profit - intenzitet poopćene dobiti
$H$	- Hamiltonian function - Hamiltonova funkcija
$l_0$	- Lagrangian, intensity of generalized cost - Lagrangeov op., intenzitet poopćenog troška
$R$	- minimum performance function [J, or $\text{Jmol}^{-1}$ ] - funkcija minimalnog predložka [J, ili $\text{Jmol}^{-1}$ ]
$S$	- entropy [ $\text{JK}^{-1}$ ] - entropija [ $\text{JK}^{-1}$ ]
$T$	- variable temperature of resource fluid [K] - varijabilna temperatura fluida izvora [K]
$T^n$	- temperature after stage $n$ [K] - temperatura nakon stupnja $n$ [K]
$T^e$	- constant temperature of environment [K] - konstantna temperatura okoliša [K]
$T'$	- Carnot temperature control [K] - Carnotova temperatura [K]
$\dot{T}$	

### Greek letters/Grčka slova

$\beta$	- coefficient, frequency constant [ $\text{s}^{-1}$ ] - koeficijent, frekvencijska konstanta [ $\text{s}^{-1}$ ]
$\lambda$	- Lagrange multiplier, time adjoint - Lagrange-ov faktor, priključno vrijeme
$\eta$	- first-law efficiency [ $-$ ] <sup>l</sup> - učinkovitost (I. glavni stavak) [ $-$ ]
$\theta$	- time interval [s,-] - vremenski interval [s,-]
$\Phi$	- factor of machine irreversibility [ $-$ ] - faktor nepovratnosti procesa u stroju [ $-$ ]
$\xi$	- intensity factor [ $-$ ] - faktor intenziteta [ $-$ ]
$\tau$	- nondimensional time or number of HTU ( $x/H_{TU}$ ) - bezdimenzijsko vrijeme ili broj jedinica prijenosa topline ( $x/H_{TU}$ ) [ $-$ ]

### Subscripts/Indeksi

$e$	- electric - električni
$k$	- k-th state variable - varijabla k- tog stanja
$m$	- molar flow - molarni tok
$1,2$	- first and second fluid - prvi i drugi fluid
	* modified cost or profit * modificirani trošak ili modificirana dobit

$t$	- $u$ rate of controlling of $T$ in time $\tau$ [K] - $u$ brzina kontroliranja $T$ u vremenu $\tau$ [K]	<u>Superscripts/Indeksi</u>
$u$	- time [s] - vrijeme [s]	$e$ - environment - okoliš
$u$	- control vector - kontrolni vektor	$I$ - initial state - početno stanje
$V_{max}$	- temperature rate control, $dT/d\tau$ [K] - kontrola brzine promijene temp, $dT/d\tau$ [K]	$n$ - stage number - broj stupnja
$W, \dot{W}$	- maximum performance funct. [J, or $Jmol^{-1}$ ] - funkcija maksimalnog predloška [J, ili $Jmol^{-1}$ ]	$f$ - initial state - početno stanje
$X$	- work and power - rad i snaga [J, $Js^{-1}$ ]	' modified quantity ' modificirani iznos
$\tilde{x}$	- state vector - vektor stanja	
$z_k$	- enlarged state vector including time - uvećani vektor stanja koji uključuje i vrijeme  - adjoint variable - priključna varijabla	

Calculations of the maximum power show that the data differ for power generated and consumed, and depend on parameters of the system, e.g., current intensity, number of mass transfer units, polarizations, electrode surface area, average chemical rate, etc. These data provide bounds for SOFC energy generators, which are more exact and informative than reversible bounds for electrochemical transformation.

Applications of thermodynamics of finite rates lead to solutions which describe various forms of bounds on power and energy production (consumption) including in dynamical cases finite-rate generalizations of the standard availabilities. In this research we treat power limits in static and dynamical energy systems driven by nonlinear fluids that are restricted in their amount or magnitude of flow, and, as such, play the role of resources.

A power limit is an upper (lower) bound on power produced (consumed) in the system. A resource is a valuable substance or energy used in a process; its value can be quantified by specifying its exergy, a maximum work that can be obtained when the resource relaxes to the equilibrium. Reversible relaxation of the resource is associated with the classical exergy. When dissipative phenomena prevail, generalized exergies are essential. In fact, generalized exergies quantify deviations of the system's efficiency from the Carnot efficiency. An exergy is obtained as the principal component of the solution to the variational problem of extremum work under suitable boundary conditions. Other components of the solution are optimal trajectory and optimal control. In purely thermal systems (those without chemical changes) the trajectory is characterized by temperature of the resource fluid,  $T(t)$ , whereas the control is Carnot temperature  $T'(t)$  defined in our

previous work [1, 2]. For chemical systems also chemical potential(s)  $\mu'(t)$  plays a role. Whenever  $T'(t)$  and  $\mu'(t)$  differ from  $T(t)$  and  $\mu(t)$  the resource relaxes

with a finite rate and with an efficiency vector different from the perfect efficiency. Only when  $T' = T$  and  $\mu' = \mu$  the efficiency is perfect, but this corresponds with an infinitely slow relaxation of the resource to the thermodynamic equilibrium with the environment fluid.

The structure of this paper is as follows. Section 2 discusses various aspects power optimization. Properties of steady systems are outlined in Sec. 3, whereas those of dynamical ones are outlined in Sec. 4. Section 5 develops quantitative analyses of resource downgrading (in the first reservoir) and outlines properties of generalized potentials for finite rates. Sections 6-8 discuss various Hamilton-Jacobi-Bellman equations (HJB equations) for optimal work functions, as solutions of power yield problems. Extensions for simple chemical systems are outlined in Sec. 9, whereas fuel cells are considered in Sects. 10-13. Section 14 analyses some power experiments in FC systems, whereas Section 15 summarizes the most important results.

The size limitation of this paper does not allow for inclusion of all derivations to make the paper self-contained, thus the reader may need to turn to some previous works, [1] - [5]. In view of the difficulties in getting analytical solutions in complex systems, approximations by difference equations and numerical approaches are treated in a separate paper [3], which, in particular, discusses the convergence of numerical algorithms with solutions of HJB equations and the role of Lagrange multipliers in dimensionality reduction. These issues are linked therein with the theory of viscosity solutions to the PD equations, discovered by Crandall and Lions in 1983 and developed in the last

two decades. The theory of viscosity solutions is nowadays the main theory concerning HJ and HJB equations. The contemporary theory is quite complete and ensures existence and uniqueness results for non-differentiable and even discontinuous solutions. Its basic premise is that, in general, value functions of variational integrals are non-smooth and hence solutions are sought in the viscosity sense [3]. Their calculation typically amounts to suitable discretization and the use of discrete dynamic programming. Viscosity solutions of HJB equations are also discussed in a recent book [14].

## 2. Finite Resources and Power Optimization

The limited amount or flow of a resource working in an engine causes a decrease of the resource potential in time (chronological or spatial). This is why studies of resource downgrading apply dynamical optimization methods. From the optimization viewpoint, the dynamical process is every one with a sequence of states, developing either in chronological time or in (spatial) holdup time. The first group refers to unsteady processes in non-stationary systems; the second group may involve steady state systems.

In a process of energy production, two resting reservoirs do interact through an energy generator (engine). In this process power flow is steady only when two reservoirs are infinite. When one, say, upper, reservoir is finite, its thermal potential must decrease in time, which is a consequence of the energy balance. Any finite reservoir is thus a resource reservoir. It is the resource property that leads to the dynamical behavior of the fluid and its relaxation to the equilibrium with an infinite lower reservoir (usually the environment).

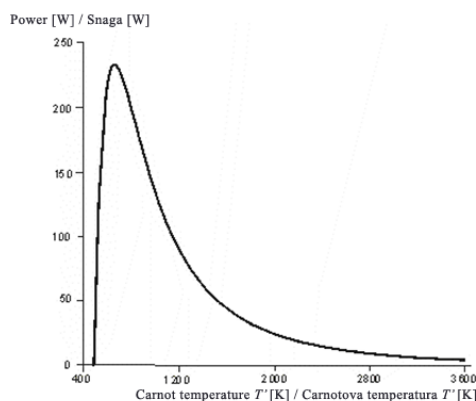
Alternatively, fluid at a steady flow can replace the resting upper reservoir. The resource downgrading is then a steady-state process in which the resource fluid flows through a pipeline or stages of a cascade and the fluid's state changes along a steady trajectory. As in the previous case, the trajectory is a curve describing the fluid's relaxation towards the equilibrium between the fluid and the lower reservoir (the environment). This is sometimes called "active relaxation" as it is associated with the simultaneous work production. It should be contrasted with "dissipative relaxation", a well-known, natural process between a body or a fluid and the environment without any power production.

Relaxation (either active or dissipative) leads to a decrease of the resource potential (i.e. temperature) in time. An inverse of the relaxation process is the one in which a body or a fluid abandons the equilibrium. This cannot be spontaneous; rather the inverse process needs a supply of external power. This is the process referred to as thermal upgrading of the resource, which can be accomplished with a heat pump.

## 3. Steady State Systems

A great deal of research on power limits published to date deals with stationary systems, in which case both reservoirs are infinite. They all refer to curves of power in terms of some control variable, such as the power curve presented in Fig.1. This case refers to steady-state analyses of the Chambadal-Novikov-Curzon-Ahlborn engine (CNCA engine [6]) in which energy exchange is described by the Newtonian law of cooling, or the Stefan-Boltzmann engine, a system with the radiation fluids and the energy exchange governed by the Stefan-Boltzmann law [7]. Due to their stationarity (caused by the infiniteness of both reservoirs), controls maximizing power are lumped to a fixed point in the state of space. In fact, for the CNCA engine, the maximum power point may be related to the optimum value of a free (unconstrained) control variable which can be efficiency  $\eta$  or Carnot temperature  $T'$ . In terms of the reservoirs temperatures  $T_1$  and  $T_2$  and the internal irreversibility factor  $\Phi$ , one finds  $T'_{opt} = (T_1 \Phi T_2)^{1/2}$  [4].

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  $P=f(T')$ .



**Figure 1.** Maximum power relaxation curve for black radiation without constraint on the temperature [8].

**Slika 1.** Relaksacijska krivulja maksimalne snage za zračenje crnog tijela bez ograničenja temperature [8].

Moreover, the method of Lagrange multipliers can successfully be applied [8]. As their elimination from a set of resulting equations is quite easy, the problem is broken down to the numerical solving of a nonlinear equation for the optimal control  $T'$ .

Finally, the so-called pseudo-Newtonian model [4, 5], which uses the state or temperature dependent heat exchange coefficient,  $\alpha(T^3)$ , omits, to a considerable extent, analytical difficulties associated with the Stefan-Boltzmann equation. Applying this model in the so-called symmetrical case, where both reservoirs are filled

up with radiation, one shows that the optimal (power maximizing) Carnot temperature of the steady radiation engine is the same as that for the CNCA engine [4]. This equation is, in fact, a good approximation under the assumption of transfer coefficients dependent solely on bulk temperatures of reservoirs.

### 4. Dynamical Systems

The evaluation of dynamical energy yield requires the knowledge of an extremal curve rather than an extremum point. This is associated with the application of variational methods (to handle functional extrema) in place of static optimization methods (to handle extrema of functions).

For example, the use of the pseudo-Newtonian model to quantify the dynamical energy yield from radiation gives rise to an extremal curve describing the radiation relaxation to the equilibrium. This curve is non-exponential, the consequence of the nonlinear properties of the relaxation dynamics. Non-exponential are also other curves describing the radiation relaxation, e.g., those obtained while using the Stefan-Boltzmann equation (symmetric and hybrid, [4,5]).

Analytical difficulties associated with dynamical optimization of nonlinear systems are severe; this is why diverse models of power yield and diverse numerical approaches are applied. The optimal (e.g. power-maximizing) relaxation curve  $T(t)$  is associated with the optimal control curve  $T'(t)$ ; they both are components of the dynamic optimization solution to a continuous problem. In the corresponding discrete problem, formulated for numerical purposes, one searches for optimal temperature sequences  $\{T^n\}$  and  $\{T'^n\}$ . Various discrete optimization methods involve: direct search, dynamic programming, discrete maximum principle, and combinations of these methods.

Minimum power supplied to the system is described in a suitable way by the function sequences  $R^n(T^n, t^n)$ , whereas maximum power produced, by the functions  $V^n(T^n, t^n)$ . The profit-type performance function  $V$  and cost-type performance function  $R$  simply differ by sign, i.e.,  $V^n(T^n, t^n) = -R^n(T^n, t^n)$ . The beginner may find the change from symbol  $V$  to symbol  $R$  and back as unnecessary and confusing. Yet, each function is positive in its own, natural regime of working ( $V$  - in the engine range and  $R$  - in the heat pump range).

Importantly, energy limits of dynamical processes are inherently connected with the exergy functions, the classical exergy and its rate-dependent extensions.

To obtain classical exergy from power functions it suffices to assume that the thermal efficiency of the system is identical with the Carnot efficiency.

On the other hand, non-Carnot efficiencies lead to generalized exergies. The latter depend not only on classical thermodynamic variables but also on their rates. These generalized exergies refer to state changes in a finite time, and can be contrasted with the classical

exergies that refer to reversible quasistatic processes evolving in time infinitely slowly. The benefit obtained from generalized exergies is that they define stronger energy limits than those predicted by classical exergies.

A systematic approach to exergies (classical or generalized) based on work functionals leads to several original results in the thermodynamics of energy systems, in particular it allows an explanation for the unknown properties of the exergy of black-body radiation or solar radiation, and it shows that the efficiency of the solar energy flux transformation is equal to the Carnot efficiency. To date this has not been a commonly accepted result, as a number of recent investigations have shown.

### 5. Towards a Finite-Rate Exergy

Two different works, the first associated with resource downgrading during its relaxation to the equilibrium and the second – with the reverse process of resource upgrading, are essential (Fig.2). During the approach to equilibrium, the engine mode takes place such that work is released, during the departure-heat-pump mode the engine mode occurs such that work is supplied. Work  $W$  delivered in the engine mode is positive by assumption (“engine convention”).

The sequence of irreversible engines (CNCA or Stefan-Boltzmann) serves to determine a rate-dependent exergy extending the classical exergy for irreversible, finite rate processes. Before maximization of a work integral, process efficiency  $\eta$  has to be expressed as a function of state  $T$  and a control, i.e. energy flux  $q$  or rate  $dT/d\tau$ , to assure the functional property (path dependence) of the work integral. The integration must be preceded by maximization of power or work at flow  $w$  (the ratio of power and flux of driving substance) to assure an optimal path.

The idea of an infinite number of infinitesimal CNCA steps, necessary for exergy calculations, is illustrated in Fig. 2.

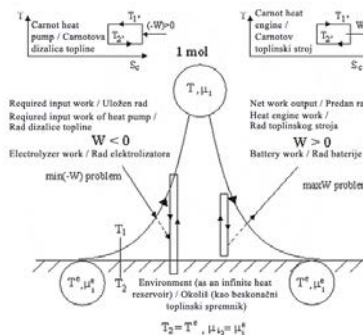


Figure 2. Two works: Limiting work produced and limiting work consumed are different in an irreversible process.

Slika 2. Dva rada: Granice predanog i utrošenog rada su različite u nepovratnom procesu

Each small step is a work-producing (consuming) stage with the energy exchange between two fluids and a thermal machine through finite “conductances”.

The optimal work is sought in the form of a potential function that depends on the end states and duration. For appropriate boundary conditions, the principal function of the variational problem of extremum work coincides with the notion of an exergy, the function that characterizes the quality of resources.

For the radiation engine, it follows from the Stefan-Boltzmann law that the effective transfer coefficient  $\alpha_1$  of the radiation fluid is necessarily temperature-dependent,  $\alpha_1 \propto T_1^3$ . The second or low- $T$  fluid represents the usual environment, as defined in the exergy theory. This fluid possesses its own boundary layer as a dissipative component, and the corresponding exchange coefficient is  $\alpha_2$ . In the physical space, the flow direction of the resource fluid is along the horizontal coordinate  $x$ . The optimizer’s task is to find an optimal temperature of the resource fluid along the path that extremizes the work consumed or delivered.

Total power obtained from an infinite number of infinitesimal engines is determined as the Lagrange functional of the following structure

$$\dot{W}[\mathbf{T}^i, \mathbf{T}^f] = \int_{t^i}^{t^f} f_0(T, T') dt = - \int_{T^i}^{T^f} \dot{G} c(T) \eta(T, T') \dot{T} dt \quad (1)$$

where  $f_0$  is power generation intensity,  $\dot{G}$  – resource flux,  $c(T)$  specific heat,  $\eta(T, T')$  – efficiency in terms of state  $T$  and control  $T'$ , further  $\mathbf{T}$  – enlarged state vector comprising state and time,  $t$  – time variable (residence time or holdup time) for the resource contacting with the heat transfer surface. Sometimes one uses a non-dimensional time  $\tau$ , identical with the so-called number of the heat transfer units. Note that, for the constant mass flow of a resource, one can extremize power per unit mass flux, i.e., the quantity of work dimension called “work at flow”. In this case Eq. (1) describes a problem of extremum work. Integrand  $f_0$  is common for both modes, yet the numerical results it generates differ by sign (positive for engine mode; “engine convention”).

When the resource flux is constant, a work functional describing the thermal exergy flux per unit flux of resource can be obtained from Eq. (1)

$$w_{\max} \frac{dT}{dt} = - \int_{T=T^i}^{T^e=T^f} c(T) \left( 1 - \frac{T^e}{T'(T, dt/dT)} \right) dT \quad (2)$$

Note that the independent variable in this equation is  $T$ , i.e., it is different than that in Eq. (1).

The function  $f_0$  in Eq. (1) contains a thermal efficiency function,  $\eta$ , described by a practical counterpart of the Carnot formula. When  $T > T^e$ , efficiency  $\eta$  decreases in the engine mode above  $\eta_C$  and increases in the heat-pump mode below  $\eta_C$ . At the limit of vanishing rates,  $dT/dt = 0$  and  $T' \rightarrow T$ . Then the

work of each mode simplifies to the common integral of the classical exergy. For the classical exergy

$$w_{\max} \frac{dT}{dt} \rightarrow 0 = - \int_{T=T^i}^{T^e=T^f} c(T) \left( 1 - \frac{T^e}{T} \right) dT \quad (3)$$

$$= h - h^e - T^e (s - s^e)$$

Nonlinearities can have thermodynamic and kinetic origins; the former refer, for example, to state dependent heat capacity,  $c(T)$ , the latter to energy exchange. Problems with linear kinetics (Newtonian heat transfer) are an important subclass. In these problems fluid’s specific work at flow,  $w$ , is described by the equation

$$w[\mathbf{T}^i, \mathbf{T}^f] = \dot{W} / \dot{G} = - \int_{T^i}^{T^f} c(T) \left( 1 - \frac{T^e}{T} \right) dT$$

$$- T^e \int_{t^i}^{t^f} c(T) \frac{(T' - T)^2}{TT} dt \quad (4)$$

where

$$\tau \equiv \frac{x}{H_{TV}} = \frac{\alpha' a_v F}{\dot{G} c} x = \frac{\alpha' a_v F v}{\dot{G} c} t = \frac{t}{\chi} \quad (5)$$

is the non-dimensional time of the process. Equation (5) assumes that a resource fluid flows with velocity  $v$  through cross-section  $F$  and contacts with the heat transfer exchange surface per unit volume  $a_v$  [1]. Quantity  $\tau$  is identical to the so-called number of heat transfer units.

Solutions to work extremum problems can be obtained by:

a) variational methods, i.e., via the Euler-Lagrange equation of variational calculus

$$\frac{\partial L}{\partial T} - \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{T}} \right) = 0 \quad (6)$$

In the example considered above, i.e., for a thermal system with linear kinetics

$$T \frac{d^2 T}{d\tau^2} - \left( \frac{dT}{d\tau} \right)^2 = 0, \quad (7)$$

which corresponds with the optimal trajectory

$$T(\tau, \tau^f, T^i, T^f) = T^i (T^f / T^i)^{\tau / \tau^f} \quad (8)$$

( $\dot{\tau} = 0$  is assumed in Eq. (8).) However, the solution of the Euler-Lagrange equation does not contain any information about the optimal work function. This is

assured by solving the Hamilton-Jacobi-Bellman equation (HJB equation, [9]).

b) dynamic programming via the HJB equation for the ‘principal function’ ( $V$  or  $R$ ), also called the extremum work function. For the linear kinetics it is considered

$$\frac{\partial V}{\partial \tau} - \max_{T'} \left\{ -\frac{\partial V}{\partial T} - c \left( 1 - \frac{T^e}{T'} \right) (T' - T) \right\} = 0. \quad (9)$$

Observe that all rates ( $f_0$  and  $f$ ) and derivatives of  $V$  are evaluated at the final state (the so-called ‘forward equation’). The extremal work function  $V$  is a function of the final state and total duration. After evaluation of optimal control and its substitution to Eq. (9), one obtains the nonlinear equation

$$\frac{\partial V}{\partial \tau} - c \left\{ \sqrt{T^e} - \sqrt{T(1 + c^{-1} \partial V / \partial T)} \right\}^2 = 0 \quad (10)$$

which is the Hamilton-Jacobi equation of the problem. Its solution can be found by the integration of work intensity along an optimal path, between the limits  $T^i$  and  $T^f$ . A reversible (path independent) part of  $V$  is the classical exergy  $A(T, T^e, 0)$ .

Details of models of multistage power production in sequences of infinitesimal engines are known from previous publications [1]-[5]. These models provide power generation functions  $f_0$  or thermal Lagrangians  $l_0 = -f_0$  and dynamical constraints. Numerical methods apply suitable discrete models, for the given rates  $f_0$  and  $f$ . An important issue is the convergence of these discrete models to continuous ones [3].

### 6. HJB Equations for Nonlinear Power Systems

We shall display here some Hamilton-Jacobi-Bellman equations for power systems described by nonlinear kinetics.

A suitable example is a radiation engine whose power integral is approximated by a pseudo-Newtonian model of radiative energy exchange associated with the optimal function

$$V(T^i, t^i, T^f, t^f) \equiv \max_{T'(t)} \left( - \int_{t^i}^{t^f} \dot{G}_m c_m \left( 1 - \Phi' \frac{T^e}{T'} \right) v(T', T) dt \right) \quad (11)$$

where  $v = \alpha(T^3)(T' - T)$ . An alternative form uses the Carnot temperature  $T'$  explicit in  $v$  [5]. Optimal power (11) can be referred to as the integral

$$\dot{W} = - \int_T^{T_0} \dot{G}_m \left( c_{hm}(T) - c_{vm}(T) \frac{T^e}{T} \right) v dt - \int_T^{T_0} T^e \dot{G}_m \left( c_{vm}(T) \left( \frac{\chi v^2}{T(T + \chi v)} + (1 - \Phi) \frac{v}{T + \chi v} \right) \right) dt \quad (12)$$

This process is described by the pseudolinear kinetics  $dT/dt = f(T, T')$  consistent with  $v = \alpha(T^3)(T' - T)$ . A general form of the HJB equation for the work function  $V$  is

$$-\frac{\partial V}{\partial t} + \max_{T'(t)} \left( f_0(T, T') - \frac{\partial V}{\partial T} f(T, T') \right) = 0 \quad (13)$$

where  $f_0$  is defined as the integrand of Eq. (11) or (12).

A more exact model or radiation conversion relaxes the assumption of the pseudo-Newtonian transfer and applies the Stefan-Boltzmann law. For a *symmetric* model of radiation conversion (both reservoirs composed of radiation),

$$\dot{W} = \int_{t^i}^{t^f} \dot{G}_c \left( 1 - \frac{\Phi T^e}{T'} \right) \beta \frac{T^a - T'^a}{(\Phi'(T'/T^e)^{a-1} + 1) T^{a-1}} dt \quad (14)$$

The coefficient  $\beta = \sigma \alpha_v c_h^{-1} (p_m^0)^{-1}$  is related to the molar constant of photons density  $p_m^0$  and the Stefan-Boltzmann constant  $\sigma$ . In the physical space, the power exponent  $a=4$  for radiation and  $a=1$  for a linear resource. With the state equation

$$\frac{dT}{dt} = -\beta \frac{T^a - T'^a}{(\Phi'(T'/T^e)^{a-1} + 1) T^{a-1}} \quad (15)$$

[5] applied in general Eq. (19) we obtain a *HJB* equation

$$-\frac{\partial V}{\partial t} + \max_{T'(t)} \left\{ \dot{G}_c \left( 1 - \Phi \frac{T^e}{T'} \right) + \frac{\partial V}{\partial T} \left( -\beta \frac{T^a - T'^a}{(\Phi'(T'/T^e)^{a-1} + 1) T^{a-1}} \right) \right\} = 0 \quad (16)$$

Dynamics (15) is a characteristic equation for Eq. (16).

For a *hybrid model* of radiation conversion (upper reservoir composed of the radiation and lower reservoir of a Newtonian fluid, [5]) the power integral is

$$\dot{W} = - \int_{t^i}^{t^f} G_c(T) \left( 1 - \frac{\Phi T^e}{(T^a + \beta^{-1} T^{a-1} u)^{1/a} + \Phi \beta^{-1} T^{a-1} u g_1 / g_2} \right) u dt \quad (17)$$



and the corresponding Hamilton-Jacobi-Bellman equation is

$$-\frac{\partial V}{\partial t'} + \max_{r(\omega)} \left\{ - \left( \dot{G}_c(T) \left( 1 - \frac{\Phi T^e}{(T^e + \beta^{-1} T^{e-1} u)^{1/\alpha}} + \Phi \beta^{-1} T^{e-1} u g_1 / g_2 \right) + \frac{\partial V}{\partial T'} \right) u \right\} = 0 \quad (18)$$

## 7. Analytical Aspects of Linear and Pseudo-Newtonian Kinetics

In all HJB equations extremized expressions there are some Hamiltonians. By applying the feedback control, the optimal driving temperature  $T'$  or other control is implemented as the quantity maximizing the Hamiltonian with respect to control  $T'$  at each point of the path. The maximization of  $H$  leads to two equations. The first expresses optimal control  $T'$  in terms of  $T$  and  $z = -\partial V / \partial T$ ; for Eq. (9) we find

$$\frac{\partial V}{\partial T} - \frac{\partial f_0(T, T')}{\partial T'} = \frac{\partial V}{\partial T} + c \left( 1 - \frac{T^e T}{T'^2} \right) = 0 \quad , \quad (19)$$

whereas the second is the original equation (9) without the maximizing operation

$$\frac{\partial V}{\partial \tau} + \frac{\partial V}{\partial T} (T' - T) + c \left( 1 - \frac{T^e}{T'} \right) (T' - T) = 0. \quad (20)$$

To obtain the optimal control function  $T'(z, T)$  one should solve the second equality in equation (19) in terms of  $T'$ . The result is the extremum Carnot control  $T'$  in terms of  $T$  and  $z = -\partial V / \partial T$ ,

$$T' = \left( \frac{T^e T}{1 + c^{-1} \partial V / \partial T} \right)^{1/2} \quad (21)$$

This formula is next substituted into (20); the result is the nonlinear Hamilton-Jacobi equation

$$-\frac{\partial V}{\partial \tau} + c T \left( \sqrt{1 + c^{-1} \partial V / \partial T} - \sqrt{T^e / T} \right)^2 = 0 \quad (22)$$

which contains the energy-like (extremum) Hamiltonian of the extremal process

$$H(T, \frac{\partial V}{\partial T}) = c T \left( \sqrt{1 + c^{-1} \partial V / \partial T} - \sqrt{T^e / T} \right)^2. \quad (23)$$

For a positively-defined  $H$ , each Hamilton-Jacobi equation for optimal work preserves the general form of autonomous equations known from analytical mechanics and the theory of optimal control.

Expressing the extremum Hamiltonian (23) in terms of state variable  $T$  and Carnot control  $T'$  yields an energy-like function satisfying the following relations

$$E(T, u) = f_0 - u \frac{\partial f_0}{\partial u} = c T^e \frac{(T' - T)^2}{T'^2} \quad (24)$$

$E$  is the Legendre transform of the work Lagrangian  $l_0 = -f_0$  with respect to the rate  $u = dT/d\tau$ .

Assuming a numerical value of the Hamiltonian, say  $h$ , one can exploit the constancy of  $H$  to eliminate  $\partial V / \partial T$ . Next, combining the equation  $H=h$  with the optimal control (21), or with an equivalent result for energy flow control  $u = T' - T$

$$u = \left( \frac{T^e T}{1 + c^{-1} \partial V / \partial T} \right)^{1/2} - T \quad (25)$$

yields the optimal rate  $u = \dot{T}$  in terms of temperature  $T$  and the Hamiltonian  $h$

$$\dot{T} = \{ \pm \sqrt{h / c T^e} (1 \pm \sqrt{h / c T^e})^{-1} \} T \quad (26)$$

A more general form of this result, which applies to systems with an internal dissipation (factor  $\Phi$ ) and applies to the pseudo-Newtonian model of radiation, is

$$\dot{T} = \left( \pm \sqrt{\frac{h_\sigma}{\Phi c_\nu(T)}} \left( 1 \pm \sqrt{\frac{h_\sigma}{\Phi c_\nu(T)}} \right)^{-1} \right) T \quad (27)$$

This result is obtained by the application of variational calculus to nonlinear radiation fluids with the temperature dependent heat capacity  $c_\nu(T) = 4a_0 T^3$ . In conclusion, the pseudo-Newtonian systems produce power relaxing with the optimal rate

$$\dot{T} = \xi(h_\sigma, T, \Phi) T \quad (28)$$

where  $\xi$ , defined on the basis of Eq. (27), is an intensity index and  $h_\sigma = h/T$ . Positive  $\xi$  refers to the heating of the resource fluid in the heat-pump mode, and the negative refers to the cooling of this fluid in the engine mode. Equations (27) and (28) describe the optimal trajectory in terms of the state variable  $T$  and the constant  $h$ . The corresponding optimal (Carnot) control is

$$T' = (1 + \xi(h_\sigma, \Phi, T)) T \quad (29)$$

The presence of the resource temperature  $T$  in the function  $\xi$  proves that, in comparison with the linear systems, the pseudo-Newtonian relaxation curve is not exponential.

## 8. Optimum Power Functions for Linear and Quasilinear Kinetics



A solution can now be found to the problem of the Hamiltonian representation of extremal work. Let us begin with linear systems. Substituting temperature control (29) with the constant  $\zeta$  into the work functional (4) and integrating along an optimal path yields the extremal work function

$$V(T^i, T^f, h) = c(T^i - T^f) - cT^e \ln \frac{T^i}{T^f} - cT^e \sqrt{\frac{h}{cT^e}} \ln \frac{T^i}{T^f} \quad (30)$$

This expression is valid for every process mode. The integration of Eq. (27), subject to end conditions  $T(\tau^j) = T^i$  and  $T(\tau^j) = T^f$ , allows expression Eq. (30) in terms of the process duration.

For the radiation  $c_v(T) = 4a_0T^3$ , where  $a_0$  is the radiation constant, an optimal trajectory solving Eqs. (27) and (29) is

$$\pm (4/3)a_0^{1/2} \Phi^{1/2} h_\sigma^{-1/2} (T^{3/2} - T^{i3/2}) - \ln(T/T^i) = \tau - \tau^i \quad (31)$$

The integration limits refer to the initial state (i) and the current state of the radiation fluid, i.e. temperatures  $T^i$  and  $T$  corresponding with  $\tau^i$  and  $\tau$ . The optimal curve (31) refers to the case when the radiation relaxation is subject to a constraint resulting from Eq. (28).

Equation (31) is associated with the entropy production term in Eq. (12). The corresponding extremal work function per unit volume of flowing radiation has the form

$$V \equiv h_v^i - h_v^f - T^e (s_v^i - s_v^f) - (4/3)a_0^{1/2} h_\sigma^{1/2} \Phi^{1/2} T^e (T^{i3/2} - T^{f3/2}) + (4/3)a_0 T^e (1 - \Phi)(T^{i3} - T^{f3}) \quad (32)$$

Also, the related exergy function, obtained from (32) after using the exergy boundary conditions, has an explicit analytical form. The classical availability of radiation at flow resides in the exergy equation in Jeter's [10] form

$$A_v^{class}(T, T^e, 0) = h_v - h_v^e - T^e (s_v - s_v^e) = h_v (1 - T^e/T) = (4/3)a_0 T^4 (1 - T^e/T) \quad (33)$$

### 9. Work Functions for Chemical Systems

The developed methodology can be extended to chemical and electrochemical engines. Here we shall make only a few basic remarks. In chemical engines mass transports participate in the transformation of chemical affinities into mechanical power [11]. Yet, as opposed to thermal machines, in chemical ones generalized reservoirs are present, capable of providing both heat and substance. When 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 finite reservoirs, however, amount and chemical potential of an active reactant decrease in time, and the considered problems are those of dynamic optimization and variational calculus.

The simplest model of a power producing chemical engine is that with an isothermal and isomeric reaction,  $A_1 - A_2 = 0$  [11]. Power and efficiency formulae for the chemical system follow from the entropy conservation and energy balance in the power-producing zone of the system (active part).

In "endoreversible" chemical engines, total entropy flux is continuous through the active zone. When a formula describing this continuity is combined with energy balance we find in the isothermal case

$$p = (\mu_1 - \mu_2)n \quad (34)$$

where  $n$  is an invariant molar flux of reagents. Process efficiency  $\zeta$  is defined as power yield per molar flux,  $n$ , i.e.,

$$\zeta = p/n = \mu_1 - \mu_2 \quad (35)$$

This efficiency is identical with the chemical affinity of the reaction in the active part of the system. While  $\zeta$  is not dimensionless, it correctly describes the system.

For a steady engine, the following function defines the chemical efficiency in terms of fuel flux  $n$  and mole fraction  $x$  (Fig. 3)

$$\zeta = \zeta_0 + RT \ln \left( \frac{x_1 - ng_1^{-1}}{ng_2^{-1} + x_2} \right) \quad (36)$$

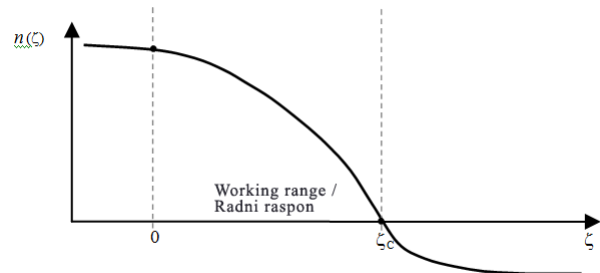


Figure 3. Fuel flux  $n$  in terms of the efficiency of power production  $\zeta$  in a chemical engine.

Slika 3. Tok goriva  $n$  u pogledu učinkovitosti proizvodnje energije  $\zeta$  u kemijskom motoru.

Equation (36) shows that an effective concentration of the reactant in the upper reservoir  $x_{1eff} = x_1 - g_1^{-1}n$  is decreased, whereas an effective concentration of the product in the lower reservoir  $x_{2eff} = x_2 + g_2^{-1}n$  is increased due to the finite mass flux. Therefore

efficiency  $\zeta$  decreases nonlinearly with  $n$ . When the effect of resistances is ignorable or flux  $n$  is very small, reversible efficiency,  $\zeta_c$ , is attained.

The power function, described by the product  $\zeta(n)n$ , exhibits a maximum for the finite value of the fuel flux,  $n$ .

Application of Eq. (36) to an unsteady system leads to the functional of an integral work

$$W = \int_{\tau_1}^{\tau_2} \left\{ \zeta_0 + RT \ln \left( \frac{X/(1+X) + dX/d\tau_1}{x_2 - jdX/d\tau_1} \right) \right\} \frac{dX}{d\tau_1} d\tau_1 \quad (37)$$

( $X=x/(1-x)$ ). Some particular properties of this functional can be deduced from the constancy of the Hamiltonian function. For low rates and large concentrations  $X$  (mole fractions  $x_1$  close to the unity) the optimal relaxation rate is approximately constant. Yet, in an arbitrary situation rates are state dependent to preserve the constancy of Hamiltonian  $H$  in Eq. (37). However, getting a complete solution for the maximum of the integral (37) requires the use of numerical approaches which usually apply Bellman's method of discrete dynamic programming.

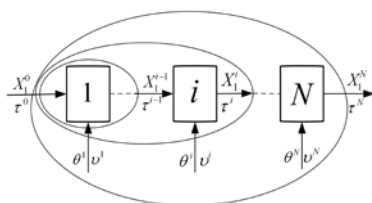
The discrete path optimality condition is represented by Bellman's recurrence equation

$$V^n(\tilde{x}^n) = \max_{u^n, \theta^n} \{ D^n(\tilde{x}^n, u^n, \theta^n) + V^{n-1}(\tilde{x}^n - \tilde{f}^n(\tilde{x}^n, u^n, \theta^n)) \} \quad (38)$$

with the control  $u=dX^n/d\tau_1$  and the extended state vector  $\tilde{x}^n \equiv (X^n, t^n)$ . The one stage profit  $D^n$  is the discrete representation of the integrand in Eq. (37). Low dimensionality of the state vector assures a good accuracy of the DP solution. Moreover, this accuracy can still be improved by introducing a Lagrange multiplier associated with the elimination of the time variable from the set of state variables. The accuracy of numerical results is then excellent. Numerical issues associated with the application of discrete models describing power systems are discussed in detail in [3].

The corresponding cascade scheme, which illustrates the principle of calculations for the power maximization in the chemical engine, is presented in Fig. 4.

Extensions of Eq. (36) are available for multireaction systems [12].



**Figure 4.** A cascade scheme for the calculation of the dynamical chemical engine by Bellman's method of dynamic programming.

**Slika 4.** Kaskadna shema računanja dinamičkog kemijskog motora Bellmanovom metodom dinamičkog programiranja.

## 10. Fuel Cells as Electrochemical Engines

A fuel cell continuously transforms a part of chemical energy into electrical energy by consuming fuel and oxidant. Fuel cells (FC) are electrochemical engines. Their role for environmental protection cannot be underestimated. The main advantage of fuel cells in comparison to heat engines is that their efficiency is not a major function of device size.

In this paper, the power maximization approach is applied for the purpose of determining power limits in imperfect fuel cells, where power decreases with current because of the prevailing effect of loss phenomena in sufficiently large electric currents.

In a previous work [1] we modeled power production and its limits in purely thermal systems with finite rates. In particular, radiation engines were analyzed as nonlinear systems governed by laws of thermodynamics and transport phenomena. Temperatures  $T$  of resource media were the only necessary variables to describe these systems. However, fuel cells are more general systems in which both temperatures  $T$  and chemical potentials  $\mu_k$  are essential. They are continuously working power generators propelled by fluxes of both energy and substances.

The basic structure of fuel cells includes the electrolyte layer in contact with a porous anode and cathode on either side. Gaseous fuels are fed continuously to the anode (negative electrode) compartment and an oxidant (i.e., oxygen from air) is fed continuously to the cathode (positive electrode) compartment. Electrochemical reactions take place at the electrodes to produce an electric current. The basic reaction is the electrochemical oxidation of fuel, usually hydrogen, and the reduction of the oxidant, usually oxygen. This principle makes a fuel cell similar to a chemical engine. In the FC process in Fig. 5, streams of fuel ( $H_2$ ) and oxidant ( $O_2$ ) interact; the process is propelled by diffusive and/or convective fluxes of heat and mass, transferred through the cell 'conductances' or boundary layers.

Power is created in the cell generator which exploits the fuel stream in contact with the anode and the oxidant stream in contact with the cathode. Both electrodes are separated by the electrolyte. As in thermal and radiation engines [4-8,13] transfer mechanisms and properties of conducting layers influence the rate of power yield.

Fuel cell systems working in the power yield mode are electrochemical flow engines propelled by chemical reactions. Their performance is determined by magnitudes and directions of participating streams and by the mechanism of electric current generation.

The lowering of voltage in a cell below its reversible value is a good measure of cell imperfection and operative cell efficiency.

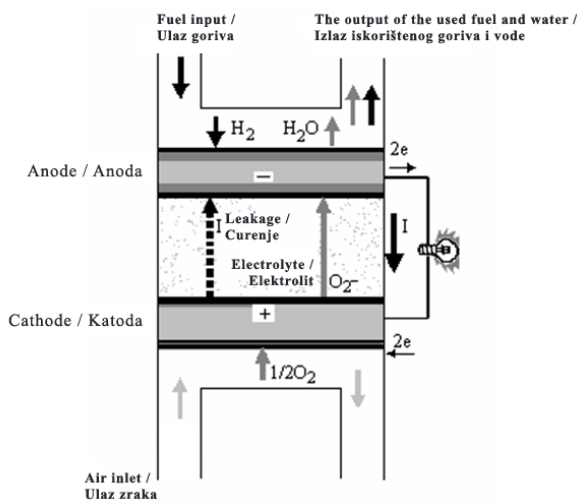


Figure 5. Principle of a solid oxide fuel cell

Slika 5. Princip rada gorivnog članka sa čvrstim oksidima kao elektrolitom (SOFC)

The goals of the FC-related sections include: (a) formulation of a thermo-electro-chemical model for imperfect fuel cells, especially for those with incomplete chemical conversions, (b) implementation of the model to simulate the behavior of high-*T* solid oxide fuel cells, (c) prediction of various losses of the voltage and their effect on the cell performance, and (d) application of fuel cell characteristics for the purpose of determining power limits.

### 11. Power Generation in Fuel Cells

Knowledge of operational voltage is required to define a cell efficiency as the ratio  $\chi = V/E$ , where *E* is the reversible cell voltage or the equilibrium cell potential. For power density in terms of  $\chi$  one obtains  $p = iE\chi$  or  $p = \chi p_{rev}$ , which means that the efficiency is equal to the ratio of the actual power to the maximum reversible power. This definition links the fuel cell efficiency with the second law, and stresses the substantial role of the operational voltage.

Assume that all incoming streams (those with “higher” Gibbs flux  $G_{in} = G_1$ ) represent a common phase of “substrates” (all system’s components in the state before the chemical transformation, index 1’). All outgoing streams (those with a “lower” Gibbs flux  $G_{out} = G_2$ ) represent the common phase of “products” (all system components in the state after the transformation, index 2’). The power expression follows from entropy conservation and energy balance in the reversible part of the system. For an isothermal reactor power yield is

$$p = \mu_{1,1} \dot{n}_{1,1} + \mu_{2,1} \dot{n}_{2,1} + \dots + \mu_{i,1} \dot{n}_{i,1} + \dots + \mu_{m,1} \dot{n}_{m,1} - \mu_{1,2} \dot{n}_{1,2} - \mu_{2,2} \dot{n}_{2,2} - \dots - \mu_{i,2} \dot{n}_{i,2} - \dots - \mu_{m,2} \dot{n}_{m,2} \quad (39)$$

This formula shows that, in a steady isothermal process, the power yield of a chemical engine system is the difference between the input and output flux of the Gibb’s function [11, 14, 15].

We can transform Eq. (39) to a pronouncing form of Eq. (40), below, specific to the case of the complete conversion. In this case the components are numbered such that species 1,2 ...*i* are substrates and species *i*+1, *i*+2 ...*m* are products. The total power yield of an isothermal multi-reaction process is

$$p = \sum_{j=1}^R \{p_j\} = \sum_{j=1}^R -\{\mu_{1,1} \nu_{1j} + \mu_{2,1} \nu_{2j} + \dots + \mu_{i,1} \nu_{ij} + \mu_{i+1,2} \nu_{i+1,j} + \dots + \mu_{m-1,2} \nu_{m-1,j} + \mu_{m,2} \nu_{mj}\} \dot{n}_j \quad (40)$$

Quantities  $\dot{n}_j$  are molar chemical fluxes of reagents, i.e. products of the electrode surface area *F* and heterogeneous rates, *r<sub>j</sub>*.

In the case of a complete conversion, power yield from the unit electrode area equals the sum of products of the affinity driving forces and the reaction rates

$$p = \sum_{j=1}^R \{\tilde{A}_j \dot{n}_j\} = F \sum_{j=1}^R \{\tilde{A}_j r_j\} \quad (41)$$

Yet, the assumption about the complete transformation of substrates into products can be relaxed, and the present paper shows how this can be done for fuel cells. By considering chemistry of systems with power production and transport phenomena, one can quantitatively estimate the effects of incomplete conversions. The related formula resembles the one which describes the effect of the internal entropy production within these systems [12].

For a single isothermal chemical reaction, the corresponding power formula which generalizes Eq. (41) to include the effect of incomplete conversions can be written in the form

$$p = (\Pi_1 - \Xi \Pi_2) \dot{n}_1 = -\frac{iA}{n_e F} \Delta g^{eff}(T, p) = -\Delta \dot{G}^{eff} \quad (42)$$

where primed quantities refer to the inputs and outputs of the chemically active zone which include the total heat flux  $\dot{Q}_1$  (involving the sensible heat flux, *q<sub>1</sub>*, and the sum of products of partial entropies and fluxes of species multiplied by the temperature *T*). The quantity  $\Pi_1$  is “one-way chemical affinity” attributed to reactants with known chemical potentials [12,14], whereas  $\dot{n}_1$  is (positive) chemical flux defined as the product of the heterogeneous reaction rate and the electrode area. Internal imperfection functions,  $\Phi$  and  $\Xi$ , are respectively related to internal entropy production

and incomplete conversion. The fraction  $\Xi$  and coefficient  $\Psi$  introduced in [12] characterize the detrimental increase of chemical potentials of reaction products caused by their dilution by remaining reactants.

The power formula of Eq. (42) generalizes the idealized power of an “endoreversible” system (with  $\Xi = 1$ ), in which case the difference  $I_{1'} - I_{2'}$  is the chemical affinity or  $-\Delta g$ . This formula is a power component which represents the power yield caused by the chemical flux  $n_1$ . In effect, electrochemical power is generated with non-ideal chemical efficiency  $\xi = I_{1'} - \Xi I_{2'}$ . For the simplest reaction,  $1 \rightleftharpoons 2$ , the efficiency equals  $\xi = \mu_{1'} - \Xi \mu_{2'}$ , which is lower than  $\mu_{1'} - \mu_{2'}$ .

Effectively, in the engine mode where  $\Xi < 1$ , the system with internal imperfections behaves as it would operate with the decreased affinity of an effective value  $I_{1'} - \Xi I_{2'}$ . Of course, the power yield is decreased due to this imperfection [16, 17].

## 12. Effect of Transport Phenomena on Power Yield

Transported energy and components drive power generation in fuel cells. Interestingly, there exists a formal link between the mathematics of thermal engines and fuel cells. To show this link, let us begin with a simple chemical engine and recall that the power producing force in an endoreversible thermal engine equals  $T_{1'} - T_{2'}$ , whereas the propelling force in the simplest chemical engine is  $\mu_{1'} - \mu_{2'}$ . (For brevity we limit ourselves to the case of a simple isomerisation reaction  $A_1 - A_2 = 0$ .)

For the bulks of the streams or reservoirs, the related differences of temperature and chemical potential are  $T_1 - T_2$  and  $\mu_1 - \mu_2$ . Since the deviations of  $T_{1'}$  and  $\mu_{1'}$  from  $T_1$  and  $\mu_1$  are of purely dissipative origin and the bulk differences  $T_1 - T_2$ , and  $\mu_1 - \mu_2$  are identical with the “open circuit” (Carnot) values for the “active” differences  $T_{1'} - T_{2'}$  and  $\mu_{1'} - \mu_{2'}$ , we may write

$$T_{1'} - T_{2'} = T_1 - T_2 - I_s(R_{1s} + R_{2s}) \quad (43)$$

$$\mu_{1'} - \mu_{2'} = \mu_1 - \mu_2 - I_n(R_{1n} + R_{2n}), \quad (44)$$

where  $I_s$  and  $I_n$  are the conserved currents of entropy and matter flowing through the energy-generating zone of the system. The indices 1 and 2 refer, respectively, to the resistances in the “upper” and “lower” part of the engine system.

The active (power producing) driving forces corresponding with Eqs. (43) and (44) are the temperature difference and chemical affinity.

Total power yield is described by the formula

$$p = (T_{1'} - T_{2'})I_s + (\mu_{1'} - \mu_{2'})I_n \quad (45)$$

$$= (T_1 - T_2)I_s + (\mu_1 - \mu_2)I_n - (R_{1s} + R_{2s})I_s^2 - (R_{1n} + R_{2n})I_n^2$$

In terms of total (summary) resistances, Eq. (45) can be written in the form

$$p = (T_{1'} - T_{2'})I_s + (\mu_{1'} - \mu_{2'})I_n \quad (46)$$

$$= (T_1 - T_2)I_s + (\mu_1 - \mu_2)I_n - R_s I_s^2 - R_n I_n^2.$$

An important problem is an extension of the above equation allowing an approximate evaluation of power limits in electro-chemical generators and fuel cells under the assumption of the simplest topology of currents flows, excluding countercurrent contacting.

We focus on the power generators described by the formalism of inert components [18, 19] rather than on the ionic description [20]. Within this formalism Eq. (45) can easily be generalized to the case of coupled transfer of heat, mass and electric charge in all the dissipative conductors of the system.

We assume, for simplicity, that, in the electrochemical case, the active (power producing) driving forces involve: one temperature difference, single chemical affinity and an operating voltage  $V = \phi_1 - \phi_2$ . (A generalization involving more affinities is obvious.)

The related power expression is

$$P = (T_{1'} - T_{2'})I_s + (\mu_{1'} - \mu_{2'})I_n + (\phi_1 - \phi_2)I_e$$

$$= (T_1 - T_2)I_s + (\mu_1 - \mu_2)I_n + (\phi_1 - \phi_2)I_e - R_{s'}I_s^2 - R_{n'}I_n^2 - R_{e'}I_e^2 \quad (47)$$

$$- R_{sn'}I_s I_n - R_{se'}I_s I_e - R_{ne'}I_n I_e.$$

This formula constitutes the simplest possible account of linear thermo-electro-chemical systems; indeed it does not contain any “topology parameter” which could possibly increase the power yield efficiency. We call the so-simplified systems “benchmark thermo-electro-chemical systems”. They are represented by Eq. (47), which excludes complex configurations of flows contacting, such as countercurrent contacts of streams (that may exist in fuel cells and increase power yield efficiencies). Systems described by Eq. (47) satisfy Ohm type or Onsager type laws linking thermodynamic fluxes and thermodynamic forces (dissipative driving forces represented by products  $R_{ik}I_k$  in Eq. (47)).

Below we shall attempt to develop a simple theory of power limits for so-standardized and so-simplified thermo-electro-chemical systems (benchmark systems). After introducing the enlarged vector of all driving potentials  $\tilde{\mu} = (T, \mu, V)$ , the flux vector of all currents  $\tilde{I} = (I_s, I_n, I_e)$ , and the overall resistance tensor  $\tilde{R}$ , Eq. (47), can be written in a simple and concise matrix-vector form

$$p = (\tilde{\mu}_1 - \tilde{\mu}_2) \cdot \tilde{I} - \tilde{R} : \tilde{I}\tilde{I} \quad (48)$$

### 13. Power Limits in Thermal Systems and Fuel Cells

While the dimensionality of the potential vector  $\tilde{\boldsymbol{\mu}}$  will certainly be much larger in some real systems, the structure of Eq. (48) will be preserved whenever this equation will be considered in the vector form.

Maximum power corresponds with the vanishing partial derivatives

$$\partial p / \partial \tilde{\mathbf{I}} = \tilde{\boldsymbol{\mu}}_1 - \tilde{\boldsymbol{\mu}}_2 - 2 \tilde{\mathbf{R}} \cdot \tilde{\mathbf{I}} = 0 \quad (49)$$

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

$$\tilde{\mathbf{I}}_{mp} = \frac{1}{2} \tilde{\mathbf{R}}^{-1} \cdot (\tilde{\boldsymbol{\mu}}_1 - \tilde{\boldsymbol{\mu}}_2) \equiv \frac{1}{2} \tilde{\mathbf{I}}_F \quad (50)$$

The above result means that in the strictly linear systems the power-maximizing current vector  $\tilde{\mathbf{I}}_{mp}$  is equal to one half of the purely dissipative current at the Fourier-Onsager point,  $\tilde{\mathbf{I}}_F$ . The latter point refers to the system's state at which no power production occurs.

Consistently, Eqs. (48) and (50) yield the following result for the maximum power limit of the system

$$p_{mp} = \frac{1}{4} (\tilde{\boldsymbol{\mu}}_1 - \tilde{\boldsymbol{\mu}}_2) \cdot \tilde{\mathbf{R}}^{-1} \cdot (\tilde{\boldsymbol{\mu}}_1 - \tilde{\boldsymbol{\mu}}_2) \quad (51)$$

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

$$p_{mp} = \frac{1}{4} \tilde{\mathbf{R}} : \tilde{\mathbf{I}}_F \tilde{\mathbf{I}}_F \quad (52)$$

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

$$p_F = \tilde{\mathbf{R}} : \tilde{\mathbf{I}}_F \tilde{\mathbf{I}}_F \quad (53)$$

Comparison of Eqs. (52) and (53) proves that, in the considered benchmark thermo-electro-chemical systems, only 25% (at the most) of power dissipated in the natural transfer process can be transformed into the noble form of the mechanical power. This is a result which, probably, cannot easily be generalized to nonlinear transfer and complex flow systems and those fuel cells in which countercurrent contacts of flows prevail (in the latter systems the considered efficiencies of power yield can be much higher than 25%).

The above analysis proves that a link exists between the mathematics of thermal engines and fuel cells, and also that the theory of fuel cells can be unified with the theory of thermal and chemical engines. Yet the topological differences of both systems may occasionally render both of them quite dissimilar.

### 14. Some Experimental Data for Fuel Cells

Already the forms of Eqs. (47) and (48) are sufficient to claim that the thermal force formula and the power formula for the thermal engine are similar to the voltage and power formulae in the fuel cell system. In this spirit, we present a brief analysis of some experimental data.

The lowering of voltage in fuel cells below the reversible voltage is a good measure of their imperfection. Yet we need to distinguish between Nernst ideal voltage  $E^0$  and/or the idle run voltage,  $E_0$ . It is the latter quantity from which all rate dependent losses of voltage should be subtracted. A number of approaches for calculating these polarization losses have been reviewed in literature by Zhao, Ou and Chen [16]. The details of calculations of the idle run voltage  $E_0$  are thoroughly discussed by Wierzbicki [17] who has implemented the Aspen Plus<sup>TM</sup> software to investigate the behavior of the SOFC-based energy system using his own theoretical model of power yield kinetics. His calculations were compared with the experimental findings of the voltage and power in a laboratory FC system.

In some situations the difference between  $E^0$  and  $E_0$  is a current independent loss which may be described by the fraction  $\mathcal{E}$  characterizing the detrimental increase of chemical potentials of products caused by their dilution by un-reacted substrates. With the concept of effective nonlinear resistances the operating voltage can be represented as the departure from the idle run voltage  $E_0$  (the quantity which replaces the reversible voltage  $E^0$  in more involved situations)

$$\begin{aligned} V &= E_0 - V_{\text{int}} = E_0 - V_{\text{act}} - V_{\text{conc}} - V_{\text{ohm}} \\ &= E_0 - I(R_{\text{act}} + R_{\text{conc}} + R_{\text{ohm}}) \end{aligned} \quad (54)$$

(Note the analogy between this equation and Eqs. (46) and (47)). The losses, called polarization, include three main sources: activation polarization ( $V_{\text{act}}$ ), ohmic polarization ( $V_{\text{ohm}}$ ), and concentration polarization ( $V_{\text{conc}}$ ). They refer to the equivalent activation resistance ( $R_{\text{act}}$ ), equivalent ohmic resistance ( $R_{\text{ohm}}$ ), and equivalent concentration resistance ( $R_{\text{conc}}$ ).

Activation and concentration polarization occur at both anode and cathode locations, while resistive polarization represents ohmic losses throughout the fuel cell. Activation polarization  $V_{\text{act}}$  is neglected in the model of ref. [17], nonetheless the power curve is typical.

As the voltage losses increase with current, the initially increasing power begins finally to decrease for



sufficiently large currents, so that the maxima of power are observed (Fig. 6). The data include the losses of the idle run attributed to the flaws in the electrode constructions and other imperfections which result in a static open circuit voltage that is in reality lower than  $E^0$ .

Moreover, in the literature there are many other experimental and theoretical examples showing power maxima in fuel cells and proving the suitability of the thermal machine theory to chemical and electrochemical systems.

The voltage equation used in Wierzbicki's SOFC calculations is:

$$V = E_0(T, p_{H_2}) - iA_R(p_{H_2}) \exp\left(\frac{\Delta E}{RT}\right) + B \ln\left(1 - \frac{i}{i_L(T, p_{H_2})}\right) \quad (55)$$

where a limiting current is defined by the equation

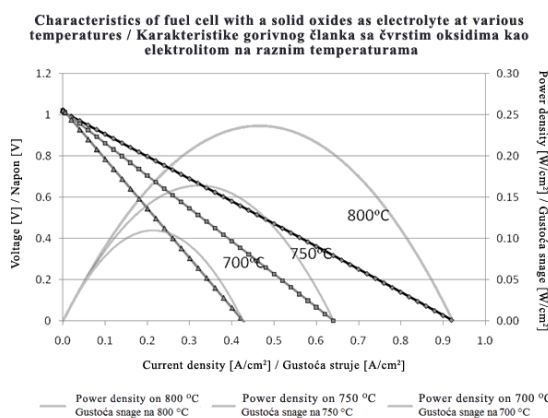
$$i_L = C_1 T^{-1} \exp\left(\frac{-E_a}{RT}\right) p_{H_2} \quad (56)$$

in which  $C_1$  is an experimentally determined parameter.

Power density is simply the product of voltage  $V$  and current density  $i$

$$p = Vi. \quad (57)$$

In an ideal situation (no losses) the cell voltage is defined by the Nernst equation. Yet, while the first term of Eq. (55) defines the voltage without load, it nonetheless takes into account the losses of the idle run, caused by flaws in electrode constructions and other imperfections. They decrease the open circuit voltage below the theoretical value. The losses include ohmic polarization and concentration polarization.



**Figure 6.** Voltage-current density and power-current density characteristics of the SOFC for various temperatures. Continuous lines represent the Aspen PlusTM calculations in testing the model versus the experiments. The lines were obtained in Wierzbicki's MsD thesis supervised by S. Sieniutycz and J. Jewulski [17]. Points refer to experiments of Wierzbicki and Jewulski at the Warsaw Institute of Energetics (Wierzbicki [17], and his ref. 18).

**Slika 6.** Karakteristike napona, gustoće struje i gustoće snage kao međusobne funkcije (napon-gustoća struje i gustoća struje-gustoća snage) na raznim temperaturama u gorivnom članku (SOFC). Kontinuirane linije predstavljaju Aspen PlusTM račune testiranja modela usporedno s eksperimentom. Linije su pronadene u Wierzbickievom doktorskom radu pisanom uz mentorstvo S. Sieniutycza i J. Jewulskija [17]. Točke se referiraju na pokuse Wierzbickija and Jewulskija na Varšavskom institutu za energetiku (Wierzbicki [17], i njegove ref. 18).

The second term of Eq. (55) quantifies ohmic losses associated with the electric resistance of electrodes and flow resistance of ions through the electrolyte. The third term refers to mass transport losses. Quantity  $i_L$  is the particular current density arising when the fuel is consumed in the reaction with the maximum rate.

Curves of power density of a SOFC fuel cell for varying hydrogen content in the fuel were also obtained by experiments of M. Blesznowski and A. Zieleniak in the Fuel Cell Department at the Institute of Power Engineering [21]. These data were applied for the purpose of the validation of the SOFC thermodynamic model in Blesznowski's forthcoming PhD thesis, supervised by the present author.

## 15. Conclusion

The models developed in this paper describe the physical and chemical performance of thermal machines and irreversible fuel cells under various operating conditions. Lowering of thermal efficiencies is attributed to differences between the temperatures and chemical potentials in the bulks and their counterparts in the circulating fluid.

Similarly, lowering of the SOFC efficiency is linked with polarizations (activation, concentration and ohmic) and incomplete conversions. The effect of incomplete conversion has been modeled assuming that substrates can remain after the reaction and that side reactions may occur.

Optimum and feasibility conditions have been obtained for a fuel cell, and discussed for some input parameters such as efficiency, power output, and electric current density of the cell.

Calculations of optimal power show that the data differ for power generated and consumed, and depend on the parameters of the system, e.g., current intensity, number of mass transfer units, polarizations, electrode surface area, average chemical rate, etc. These data provide bounds for SOFC energy generators, which are more exact and informative than the reversible bounds for electrochemical transformation.

The power production bounds (limits) obtained in this paper are enhanced in comparison with those predicted by classical thermodynamics. As opposed to classical thermodynamics, these power bounds depend not only on changes of the thermodynamic state of participating resources but also on process irreversibilities, process

direction and the mechanism of heat and mass transfer. In fact, this research provides enhanced power bounds.

In thermostatics, the bound on the work produced coincides with that on the work consumed. The generalized thermo-kinetic bounds, obtained here, are stronger than those predicted by thermostatics. 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.

The general theoretical framework of the present paper is consistent with the ideas developed in the fields called "finite time thermodynamics" and "entropy generation minimization", as presented, for example, in the books by de Vos [7], Sieniutycz and Jeżowski [14], Bejan and Mamut [22] and others. Occasionally, this framework may involve classical exergy analyses such as those presented in the books by Szargut, Morris and Steward [23], Dincer and Rosen [24] and other sources of this sort. We also would like to point out some of the related papers already published in the present journal (*Strojarstvo*, [25]), which deal with the numerical investigation of the effects of porous properties on the performance of fuel cells and which can provide further valuable information regarding that subject in the present work.

### Acknowledgements

This research was supported by a grant entitled *Thermodynamics and Optimization of Chemical and Electrochemical Energy Generators with Applications to Fuel Cells*, from The Polish Ministry of Science (grant NN208 019434).

### REFERENCES

- [1] SIENIUTYCZ, S.: *A synthesis of thermodynamic models unifying traditional and work-driven operations with heat and mass exchange*, Open Systems & Information Dynamics, Vol. 10, 2003, pp. 31-49.
- [2] SIENIUTYCZ, S.: *Carnot controls to unify traditional and work-assisted operations with heat & mass transfer*, International J. of Applied Thermodynamics, Vol. 6, 2003, pp. 59-67.
- [3] SIENIUTYCZ, S.: *Dynamic programming and Lagrange multipliers for active relaxation of fluids in non-equilibrium systems*, Applied Mathematical Modeling, Vol. 33, 2009, pp. 1457-1478.
- [4] SIENIUTYCZ, S., KURAN, P.: *Nonlinear models for mechanical energy production in imperfect generators driven by thermal or solar energy*, Intern. J. Heat Mass Transfer, Vol. 48, 2005, pp.719-730.
- [5] SIENIUTYCZ, S., KURAN, P.: *Modeling thermal behavior and work flux in finite-rate systems with radiation*, Intern. J. Heat Mass Transfer, Vol. 49, 2006, pp.3264-3283.
- [6] CURZON F.L., AHLBORN, B.: *Efficiency of Carnot engine at maximum power output*, American J. Phys., Vol. 43, 1975, pp. 22-24, 1975.
- [7] DE VOS, A.: *Endoreversible thermodynamics of solar energy conversion*, Oxford University Press, Oxford 1994.
- [8] KURAN, P.: *Nonlinear models of production of mechanical energy in non-ideal generators driven by thermal or solar energy*, PhD thesis, Warsaw University of Technology, Warsaw 2006.
- [9] BELLMAN, R. E.: *Adaptive control processes: a guided tour*, Princeton University Press, Princeton, 1961, pp.1-35.
- [10] JETER, J., *Maximum conversion efficiency for the utilization of direct solar radiation*, Solar Energy, Vol. 26, 1981, pp. 231-236.
- [11] SIENIUTYCZ, S.: *An analysis of power and entropy generation in a chemical engine*, Intern. J. of Heat and Mass Transfer, Vol. 51, 2008, pp. 5859-5871.
- [12] SIENIUTYCZ, S.: *Complex chemical systems with power production driven by mass transfer*, Intern. J. of Heat and Mass Transfer, Vol. 52, 2009, pp. 2453-2465.
- [13] SIENIUTYCZ, S.: *Dynamic programming and Lagrange multipliers for active relaxation of resources in non-equilibrium systems*, Applied Mathematical Modeling, Vol. 33, 2009, pp. 1457-1478.
- [14] SIENIUTYCZ, S., JEŻOWSKI, J.: *Energy optimization in process systems*, Elsevier, Oxford, 2009.
- [15] TSIRLIN, A. M., KAZAKOV, V., MIRONOVA, V. A., AMELKIN, S. A.: *Finite-time thermodynamics: conditions of minimal dissipation for thermodynamic process*, Physical Review E, Vol. 58, 1998, pp. 215-223.
- [16] ZHAO, Y., OU, C., CHEN, J.: *A new analytical approach to model and evaluate the performance of a class of irreversible fuel cells*, International Journal of Hydrogen Energy, Vol. 33, 2008, pp. 4161- 4170.
- [17] WIERZBICKI, M.: *Optimization of SOFC based energy system using Aspen Plus<sup>TM</sup>*, MsD Thesis supervised by S. Sieniutycz (Faculty of Chemical and Process Engineering, Warsaw University of Technology) and J. Jewulski (Laboratory of Fuel Cells, Institute of Energetics, Warsaw), Warszawa 2009.
- [18] SUNDHEIM, B.R.: *Transport properties of liquid electrolytes*, p.p. 165-254 in: B.R. Sundheim, ed., Fused Salts, Mc Graw Hill, New York, 1964.
- [19] EKMAN, A., LIUKKONEN, S., KONTTURI, K.: *Diffusion and electric conduction in multicomponent electrolyte systems*, Electrochimica Acta, Vol. 23, 1978, pp. 243-250.
- [20] NEWMAN, J., *Electrochemical systems*, Prentice Hall, Englewood Cliffs, 1973.
- [21] SIENIUTYCZ, S., SZWAST, Z., KURAN, P., POŚWIATA, A., ZALEWSKI, M., PRZEKOP, R., BLESZNOWSKI, M.: *Thermodynamics and optimization of chemical and electrochemical energy generators with applications to fuel cells*, Res. Report NN208019434 for the period 16.05.2008-15.05.2011, Warsaw TU, Faculty of Chemical and Process Engineering, Warszawa 2011.
- [22] BEJAN, A., MAMUT, E., Eds.: *Thermodynamic optimization of complex energy systems*, Kluwer Academic Publishers, Dordrecht, 1999.
- [23] SZARGUT, J., MORRIS D., STEWARD, F. R.: *Exergy analysis of thermal, chemical and metallurgical processes*, Hemisphere Publishing Corporation, New York, 1988.



- [24] DINCER I., ROSEN, M.A.: *Exergy, energy, environment and sustainable development*, Elsevier, Oxford, 2007.
- [25] GULAN, U., TURKOGLU, H.: *Numerical investigation of effects of porous layer properties and thickness on performance of PEMFC*, Strojarstvo: Journal for Theory and Application in Mechanical Engineering, Vol.52 (No.5), 2010, pp. 507 -516.