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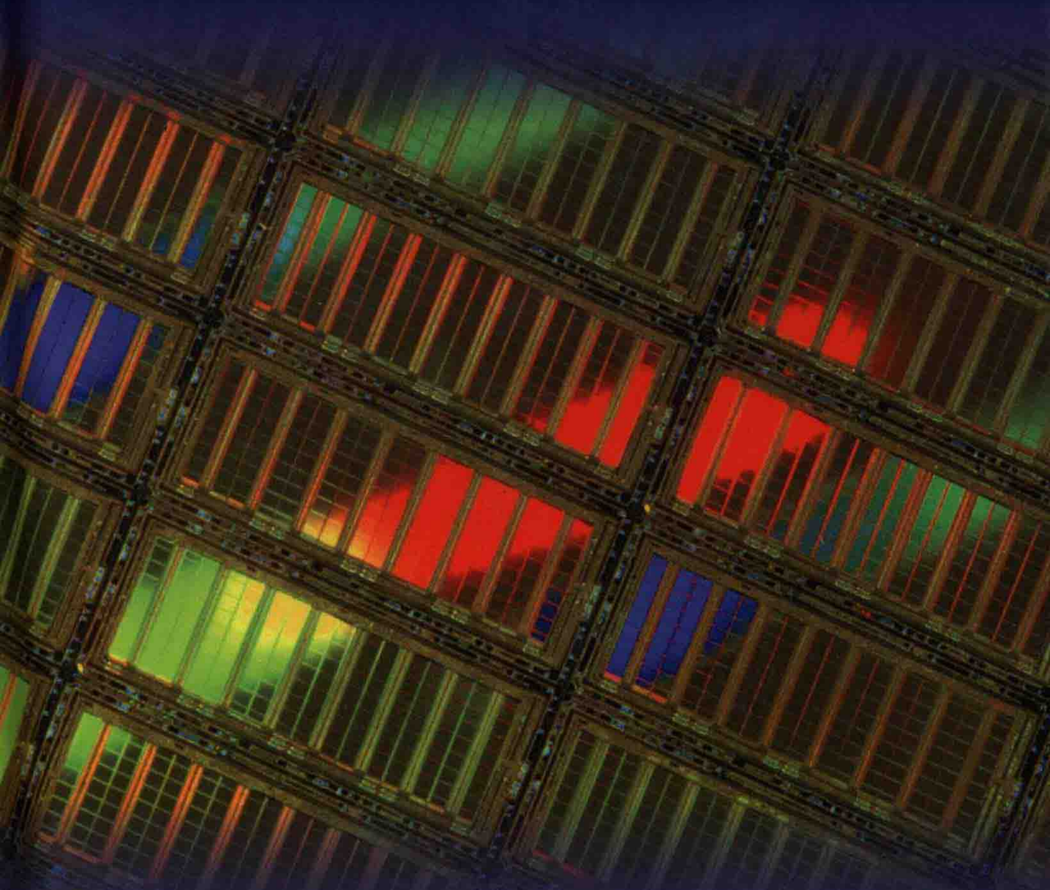

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# Energy Optimization in Process Systems and Fuel Cells

## Second Edition

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# Energy Optimization in Process Systems and Fuel Cells

# Preface

Energy systems are optimized in order to satisfy several primary goals. The first goal (Chapters 3–10 of this book) requires searching for limiting values of some important physical quantities, e.g. limiting power, minimum heat supply, maximum final concentration of a key component, etc. The second goal (Chapters 8 and 11), perhaps the most practical, applies profit or cost analyses to find economically (or exergo-economically) optimal solutions. The third goal (Chapters 12–20) pursues optimal solutions assuring the best system integration.

Optimizations toward energy limits arise in various chemical and mechanical engineering systems (heat and mass exchangers, thermal networks, energy converters, recovery & storage units, solar collectors, separators, chemical reactors, etc.). Associated energy problems are those with conversion, generation, accumulation and transmission of energy. These problems are treated by mathematical methods of optimization such as: nonlinear programming with continuous and mixed variables, dynamic programming, and Pontryagin's maximum principles, in their discrete and continuous versions. The considered processes occur in a finite time and with equipment of finite dimension. Penalties on rate and duration and optimal performance criteria of potential type (obtained within exergy or economic approaches) are effective.

In Chapters 3–10 we define and analyze thermodynamic limits for various traditional and work-assisted processes with finite rates that are important in chemical and mechanical engineering, with a few excursions into ecology and biology. The thermodynamic limits are expressed either as maxima of power or in terms of classical or generalized exergies, where the latter include some rate penalties. We consider processes with heat, work and mass transfer that occur in equipment of finite dimensions and define energy limits of various ranks for these processes. In particular, we show that the problem of energy limits is a purely physical problem that may be stated without any relation to economics. The considered processes include heat-mechanical operations (and are found in heat and mass exchangers), thermal networks, energy converters, energy recovery units, chemical reactors, and separation units. Simple exergo-economics fluidized systems are investigated as those preserving large transfer or reaction area per unit volume. Our analysis is based on the condition that in order to make the results of thermodynamic analyses applicable in industry, it is the thermodynamic limit, not the maximum of thermodynamic efficiency, which must be overcome for prescribed process requirements. Our approach analyzes the physical problem of energy limits as a new direction in nonequilibrium thermodynamics of practical devices in which the optimal control theory is both essential and helpful. Control 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 definition in reversible systems and classical problems of extremum work are pointed out. Practical problems and illustrative examples are selected in order to give an outline of applications. Considerable simplification in analysis of complicated thermal/chemical machines is achieved when some special controls (Carnot variables, $T'$ and $\mu'$—see Chapters 3 and 9) are applied. In particular, the description of classical and work-assisted heat & mass exchangers is unified.

Conclusions may be formulated regarding limits on mechanical energy yield in practical nonlinear systems. It is shown that these limits differ for power generated and power consumed, and that they depend on global working parameters of the system (e.g. total number of heat transfer units, imperfection factor of power generators, average process rates, number of process stages, etc.). New results constitute, between others, limits on multistage production (consumption) of power in nonlinear thermal and chemical devices. They characterize dynamical extrema of power yield (or consumption) for a finite number of stages or a finite time of the resource exploitation. Frequently, these systems are governed by nonlinear kinetics, as in the case of radiation or chemical/electrochemical engines. The generalization of this problem takes into account contribution of transport processes and imperfections of power generators, and includes the effect of drying out the resources of energy and matter. These solutions provide design factors for energy generators that are stronger than the familiar thermostatic bounds (i.e. classical limits for the energy transformation).

Since electrochemical power generation can occur in both thermochemical and biological systems, in this volume fuel cells are treated jointly for chemical and biological systems (Chapter 10). First, the power-efficiency thermodynamics of classical chemical reaction driven fuel cells is developed and power limits are analyzed. Next, two categories of biological fuel cells are considered: enzymatic and microbiological. The former, because of the biocatalyst immobilization, offer high current densities and possibilities of the device miniaturization. The latter, exploiting living organisms, can work for prolonged time and use complex substrates. Bacteria are regarded as self-reproducing catalysts, the property which assures continual production of power. For developing bio-systems, selected evolution examples are briefly considered to determine how system properties change when an evolving organism increases its number of elements (organs or limbs). In some biological systems, evolutionary growth in the number of organs or limbs is accompanied by catastrophes caused by abrupt changes in qualitative properties of the organism or its part. These examples substantiate Williston's law known in the evolution theory, which predicts the evolutionary tendency to reduce number of similar organs or limbs along with a simultaneous modification (specialization) of elements retained by the organism.

This book applies optimization approaches found in second law analysis, finite time thermodynamics, entropy generation minimization, exergo-economics, and system engineering to simulation and optimization of various energy processes. This book promotes systematic thermo-economic methodology and its underlying thermodynamic and economic foundations in various physical and engineering systems. It is a modern approach to energy systems which applies methods of optimization and thermal integration to obtain optimal controls and optimal costs, sometimes in the form of certain potentials depending on the process state, duration and number of stages. The approach, which is common for both discrete and continuous processes, derives optimal solutions by using mathematical models coming from thermophysics, engineering, electrochemistry and economics. It deals with thermodynamic or thermo-economic costs expressed in terms of exergy input, dissipated exergy, or certain extensions of these quantities including time or rate penalties, investment and other economic factors.

When a practical device, apparatus or a machine performs certain engineering tasks (or a 'duty') it is often reasonable to ask about a corresponding lower bound on energy consumption or, if applicable, an upper bound on energy production. The first case occurs in separators, including dryers, the second – in energy generators or engines. Regardless of the economic cost (that may be in some cases quite high or even exceeding an acceptable value), these factors —technical limits—inform an engineer about the system's potential; that of minimum necessary consumption or that of maximum possible yield. Thus, they don't represent economically optimal solutions but rather define limiting extreme possibilities of the system. Technical limits, in particular thermodynamic ones, are important factors in engineering design. In fact, no design is possible that could violate these limits without changes in the system's duty. Classical thermodynamics is capable of providing energy limits in terms of exergy changes. However, they are often too distant from reality; real energy consumption can be much higher than the lower bound and/or real energy yield can be much lower than the upper bound. Yet, by introducing rate-dependent factors, irreversible thermodynamics offer enhanced limits that are closer to reality.

Limits for finite resources are associated with the notion of exergy. They refer either to a sequential relaxation of a resource to the environment (engine mode), or to resources being upgraded in the process going in the inverse direction (heat-pump mode). To deal with these dynamical processes one must first find a general formula for the converter's efficiency and, then, evaluate a limiting work via an optimization. In an irreversible case this limiting work is an extension of the classical work potential. The real work to be optimized is a cumulative effect obtained from a system composed of: a resource fluid at flow (traditional medium or radiation), a set of sequentially arranged engines, and an infinite reservoir.

During the approach to the equilibrium, power is released in sequential engine modes; during the departure—it is supplied in heat-pump modes. In an engine mode a fluid's potential (e.g. temperature $T$) decreases, to the bath temperature. In a heat-pump mode direction is inverted and the fluid is thermally upgraded. The work ($W$) delivered in the engine mode is positive by assumption. In the heat-pump mode $W$ is negative, or positive work ($-W$) is supplied to the system. To calculate a generalized exergy, optimization problems are solved, for maximum of work yield [max $W$] and for minimum of the work supply [min ($-W$)]. The generalized exergy emerges as a function of usual thermal coordinates and a rate or dissipation index, $h_\sigma$ (in fact, the Hamiltonian value of the extreme process). In some examples we focus on limits evaluated for the work from solar radiation. Limits related analyses answer then the question about a maximum fraction of solar energy that can be converted into mechanical energy. They lead to estimates of maximum work released from a radiation engine and minimum work supplied to a heat pump. Knowing the latter limit, one can calculate lowest supply of solar or microwave energy to a dryer or other separator.

Classical exergy defines bounds on work delivered from (supplied to) slow, reversible processes (Berry et al. 2000). For such bounds the magnitude of the work delivered during a reversible approach to the equilibrium is equal to that of the work supplied when initial and final states are inverted, i.e. when the second process reverses to the first. Yet, bounds predicted by generalized exergies (i.e. those for finite rate processes) are not reversible. In fact, they are different for engine and heat-pump modes. While the reversibility property is lost for a generalized exergy, its bounds are stronger than classical thermostatic bounds.

A remarkable result discussed in this book, is a formal analogy between expressions describing entropy production in operations with thermal machines and in those in traditional heat and mass exchangers, provided that both sorts of operations are described in terms of a suitable control variable. In fact, the analogy emerges when the modeling involves a special control variable $T'$, called Carnot temperature, which represents the joint effect of upper and lower temperatures of the circulating medium, $T_1'$ and $T_2'$. Since these temperatures are linked by the internal entropy balance (through the power generating part of the machine), there is effectively only one free control, which is just Carnot temperature $T'$ (Chapter 3). When mass transfer is included (Chapter 9), a similar control can be introduced which is Carnot chemical potential $\mu'$, a quantity suitable in optimization of diffusion and chemical engines. A detailed formal treatment of these issues is given in a recent publication, (Sieniutycz, 2011f).

This book fills a gap in teaching the process optimization and process integration in energy systems by using scientific information contained in thermodynamics, kinetics, economics and systems theory. Despite numerous works on energy and process integration in real systems (of finite size) appearing regularly in many research journals, no synthesizing treatment linking energy systems optimization with process integration exists so far in the literature. In this book, optimization problems arising in various chemical and mechanical engineering systems (heat and mass exchangers, thermal and water networks, energy converters, recovery units, solar collectors, and chemical separators) are discussed. The corresponding processes run with conversion, generation, accumulation and transmission of energy or substance, and their optimization requires advanced mathematical methods of discrete and continuous optimization and system integration. The methods commonly applied are: nonlinear programming, dynamic programming, variational calculus, Hamilton-Jacobi-Bellman theory, Pontryagin's maximum principles and methods of process integration. Synthesis of thermodynamics, kinetics and economics is achieved through exergo-economic and thermo-kinetic approaches, generalizing classical thermodynamic approaches by taking into account constrained rates, finite sizes of apparatus, environmental constraints, and economic factors.

Heat energy and process water integration within a total site significantly reduces production costs; in particular, costs of utilities commonly applied in process systems such as in the chemical industry and relative branches including waste treatment facilities for environmental protection. However, the presented approaches are also aimed at the total annual cost of subsystems of interest. The integration (Chapters 12–20) requires systematic approaches to design and optimize heat exchange and water networks (HEN and WN). The presentation of these issues, in this book, starts with basic insight-based Pinch Technology for heat recovery to provide problem understanding and, also, short-cut solution techniques. Then systematic, optimization-based, sequential, and simultaneous approaches to design HEN and WN are described. The approaches show how to identify application-specific constraints and requirements and incorporate them into solutions. They also clarify available computational methods. The authors focus on a class of methods that are founded on superstructure concepts. This is the result of their opinion, that such approaches are able to deal efficiently with complex industrial cases. Suitable optimization techniques should be used to achieve the aims. In the case of HEN design problems, special consideration is given to the targeting stage because of its importance at the various levels of the complex process of system design. Also, targets for HEN can be calculated for large scale industrial cases using widely available computer aids. In particular, an advanced simultaneous approach is addressed that generates optimal heat load distribution with regard to total cost. This outcome can be used to devise the final design of HEN in some cases. Selected, advanced methods for HEN synthesis and retrofit are presented. The material here is based on a thorough review of recent literature, with some innovative approaches developed by the authors. In particular a method is given to retrofit a HEN design consisting of standard heat exchangers. The approach employs Genetic Algorithms. In the case of WN design, an innovative approach based on the stochastic optimization method is described. The approach accounts for both grass roots and revamp design scenarios. It is also applicable for calculating targets such as minimum freshwater usage for various raw water sources. Some approaches for HEN and WN design are solved with stochastic/meta-heuristic optimization techniques. The tools are applicable for general nonlinear optimization problems. Hence, in Chapter 1, a separate Section 1.6 contains detailed procedures for these optimization techniques such as Adaptive Random Search, Simulated Annealing, and Genetic Algorithms.

To date, no complete synthesizing treatment of energy systems optimization has been published—in spite of numerous works on energy appearing regularly in many research journals. Yet, a list of some earlier books on optimization or thermal integration can be quoted: (Aris 1961,1964; Beveridge and Schechter 1970; Rosenbrock and Storey 1966; Floudas 1995; Shenoy 1995; El-Halwagi 1997; Biegler, Grossman and Westerberg 1997; Edgar, Himmelblau and Lasdon 2001; Peters, Timmerhaus and West 2003; Smith 2005; Seider, Seader and

Lewin 2004). More recently, several original books appeared (Feidt, 2006; Jaluria 2007; Dincer and Rosen 2007; Mench 2008; Logan 2008), which include, between others, electrochemical systems and fuel cells. While all these books are of considerable value, they do not contain important recent results achieved in the fields of energy optimization and process integration. New results have been obtained for thermal and solar engines, thermal and water networks, and process separators. More recent books amongst those cited above, concentrate on specific topics, such as heat integration (Shenoy, 1995) or mass integration (El-Halwagi 1997, 2005), theory and application of deterministic optimization techniques (Floudas 1995 and Edgar et al. 2001). Some are textbooks for undergraduate students with only basic information on advanced design approaches (e.g. Smith 2005). Some concentrate primarily on simulator application, (e.g. Seider et al. 2004). Though these references are relatively recent, they do not entirely cover new developments on process integration.

Since the important lifecycle problems are omitted in the present book and majority of books cited above, we refer the reader to the excellent paper by MacLean and Lave (2003) on evaluating automobile fuel/propulsion system technologies. The authors of that paper examine the life cycle implications of a wide range of fuels and propulsion systems that could power cars and light trucks in the US and Canada over the next two to three decades, including fossil fuels, hydrogen and electricity, hybrid electric propulsion options, and fuel cells. They review recent studies to evaluate the environmental, performance, and cost characteristics of fuel/propulsion technology combinations that are currently available or will be available in the next few decades.

While nonlinear programming, optimal control, and system integration techniques are basic mathematical tools, this book addresses applied energy problems in the context of the underlying thermodynamics and exergoeconomics. This book can be used as a basic or supplementary text in courses on optimization and variational calculus, engineering thermodynamics, and system integration. As a text for further research, it should attract engineers and scientists working in various branches of applied thermodynamics and applied mathematics, especially those interested in the energy generation, conversion, heat & mass transfer, separations, optimal control, fuel cells, biosystems, etc. Applied mathematicians will welcome a relatively new approach to the theory of discrete processes involving an optimization algorithm with a Hamiltonian constant along the discrete trajectory and its generalization for systems nonlinear in time intervals (which may arise for some special discretizing of underlying continuous models). They should also appreciate numerous commentaries on convergence of discrete dynamic programming algorithms to viscosity solutions of Hamilton–Jacobi–Bellman equations.

This book can be used as a basic or supplementary text in the following courses:

- optimization and variational methods in engineering (undergraduate)
- technical thermodynamics and industrial energetics (undergraduate)

- alternative and unconventional energy sources (undergraduate)
- heat recovery and energy savings (graduate)
- separation operations and systems (graduate)
- thermo-economics of solar energy conversion (graduate)
- thermodynamics of imperfect fuel cell systems (graduate)

The content organization of this book is as follows: in Chapters 1 and 2, an outline of static and dynamic optimization is presented, focusing on methods applied in the examples considered in the book. Chapter 3 treats power limits for steady thermal engines and heat pumps. Chapter 4 develops power optimization theory for dynamic systems modelled as multistage cascades; cascade models are applied to handle the dynamical behavior of engines and heat pumps when the resource reservoir is finite, and the power generation cannot be sustained at a steady rate. Chapters 5–7 analyze various dynamical energy systems characterized by nonlinear models, in particular radiation systems. In Chapter 8, thermally driven and work-assisted drying operations are considered; in particular, the use of an irreversible heat-pump to upgrade a heating medium entering the dryer is described. Chapter 9 treats optimal power yield in chemical reactors, and Chapter 10—efficiencies and power limits in electrochemical and biological fuel cells, and also some related evolutionary systems. Chapter 11 outlines system analyses in thermal and chemical engineering and contains a discussion of the issues at the interface of energy limits, exergo-economics and ecology. Various aspects of the process integration are treated in Chapters 12–20. First, in Chapter 12, introductory remarks are given on heat and water integration in a context of total site integration. A brief literature overview is also supplied. The next chapter addresses the basics of heat Pinch Technology. Chapter 14 gives the foundation for the targeting stage of HEN design. The following chapters address the most important targets in sequence: first maximum heat recovery with systematic tools in Chapter 15; then, in Chapter 16, the minimum number of units and minimum area targets. Approaches for simultaneous targeting are analyzed in Chapter 17; the HEN design problem is dealt with in two chapters: grass roots design in Chapter 18, and HEN retrofit in Chapter 19. Finally, Chapter 20 contains the description of both the insight based and systematic approaches for WN targeting and design.

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# Contents