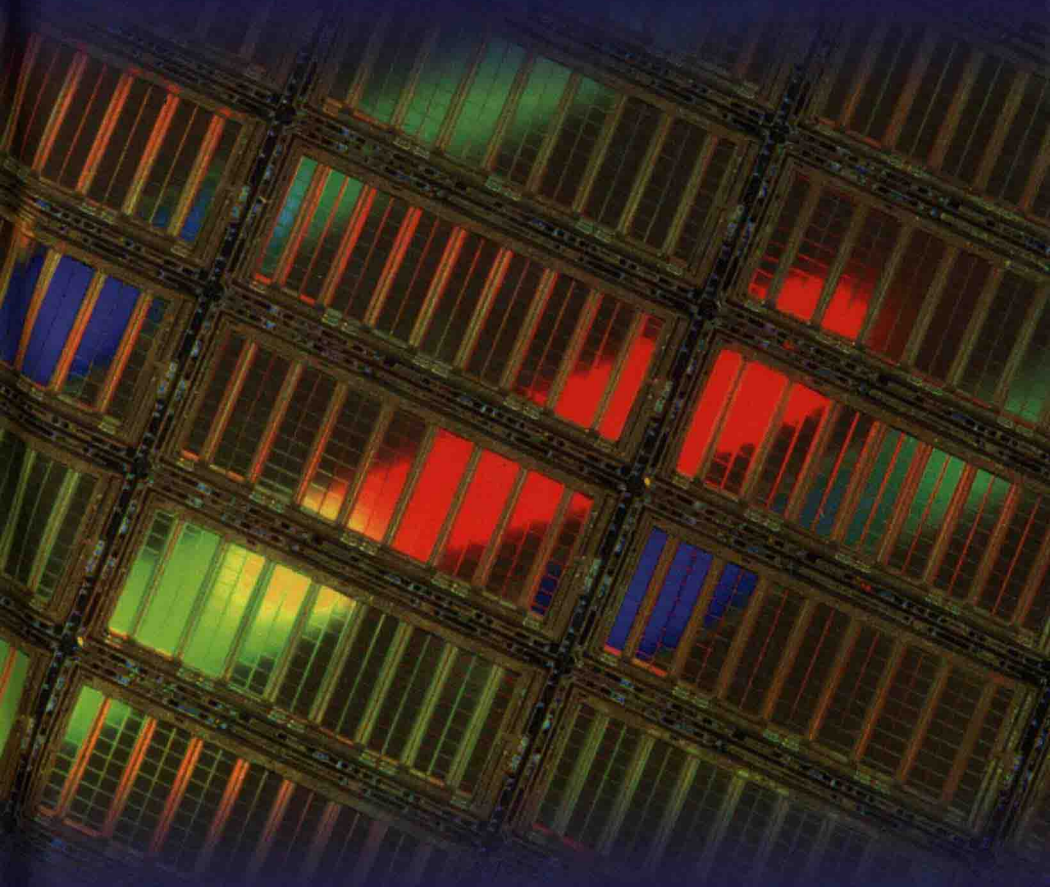
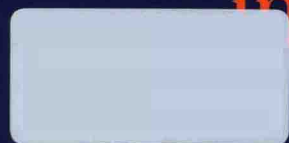


Second Edition

Energy Optimization in Process Systems and Fuel Cells



Stanisław Sieniutycz and Jacek Jeżowski†

Energy Optimization in Process Systems and Fuel Cells

Second Edition

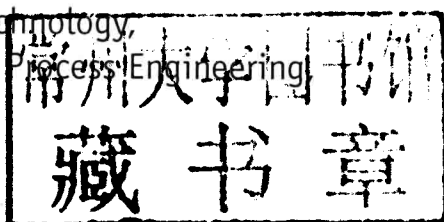
By

Stanisław Sieniutycz

Warsaw University of Technology,
Faculty of Chemical and Process Engineering,
Warsaw, Poland

Jacek Jeżowski†

Rzeszów University of Technology,
Department of Chemical and Process Engineering,
Rzeszów, Poland



ELSEVIER

AMSTERDAM • BOSTON • HEIDELBERG • LONDON • NEW YORK • OXFORD
• PARIS • SAN DIEGO • SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

Elsevier

Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK
225 Wyman Street, Waltham, MA 02451, USA
525 B Street, Suite 1800, San Diego, CA 92101-4495, USA

Second Edition

Copyright © 2013, 2009 Elsevier Ltd. All rights reserved.

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means electronic, mechanical, photocopying, recording or otherwise without the prior written permission of the publisher.

Permissions may be sought directly from Elsevier's Science & Technology Rights Department in Oxford, UK: phone (+44) (0) 1865 843830; fax (+44) (0) 1865 853333; email: permissions@elsevier.com. Alternatively you can submit your request online by visiting the Elsevier web site at <http://elsevier.com/locate/permissions>, and selecting Obtaining permission to use Elsevier material

Notice

No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

ISBN: 978-0-08-098221-2

For information on all Elsevier publications
visit our web site at store.elsevier.com

This book has been manufactured using Print On Demand technology. Each copy is produced to order and is limited to black ink. The online version of this book will show color figures where appropriate.

Working together to grow
libraries in developing countries

www.elsevier.com | www.bookaid.org | www.sabre.org

ELSEVIER

BOOK AID
International

Sabre Foundation

Transferred to Digital Printing in 2013

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 μ' —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_{σ} (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 μ' , 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.

Acknowledgments

Acknowledgments constitute the last and most pleasant part of this preface. The authors express their gratitude to the Polish Committee of National Research (KBN); under the auspices of which a considerable part of their own research discussed in the book—was performed, in the framework of two grants: grant 3 T09C 063 16 (Thermodynamics of development of energy systems with applications to thermal machines and living organisms) and grant 3 T09C 02426 (Non-equilibrium thermodynamics and optimization of chemical reactions in physical and biological systems). Chapter 9 on chemical reactors was prepared in the framework of the current grant N N208 019434 entitled “Thermodynamics and optimization of chemical and electrochemical energy generators with applications to fuel cells” supported by Polish Ministry of Science. A critical part of writing any book is the process of reviewing, thus the authors are very much obliged to the researchers who patiently helped them read through various chapters and who made valuable suggestions. In preparing this book, the authors received help and guidance from: Viorel Badescu (Polytechnic University of Bucharest, Romania), Miguel J. Bagajewicz, (University of Oklahoma, USA.), R. Steven Berry (University of Chicago, USA.) Roman Bochenek, Alina Jeżowska and Grzegorz Poplewski (Rzeszow University of Technology), Lingen Chen (Naval University of Engineering, Wuhan, China), Guoxing Lin (Physics, Xiamen University, P. R. China), Günter Wozny (TU Berlin, Germany), Vladimir Kazakov (University of Technology, Sydney), Andrzej Kraslawski (Lappeenranta University of Technology, Finland), Piotr Kuran, Artur Poświata and Zbigniew Szewast (Warsaw University of Technology), Elżbieta Sieniutycz (University of Warsaw), Anatolij M. Tsirlin (Pereslavl-Zalessky, Russia), Andrzej Ziębik (Silesian University of Technology, Gliwice), and Anita Koch (Acquisition Editor) and Anusha Sambamoorthy (Project Manager) from Elsevier. Special thanks are due to Professor A. Ziębik who agreed that the authors exploit, practically in extenso, his 1996 paper System analysis in thermal engineering, published in Archives of Thermodynamics 17: 81–97, which now constitutes an essential part of Chapter 11 of this book. We also acknowledge the consent of the Institute of Fluid Flow Machinery Press in Gdańsk, Poland, the Publisher of Archives of Thermodynamics. Finally, appreciation goes to the book production team in Elsevier for their cooperation, patience, and courtesy.

Contents

Preface	xi
Acknowledgments	xix
Chapter 1: Brief review of static optimization methods	1
1.1. Introduction: Significance of Mathematical Models	1
1.2. Unconstrained Problems	4
1.3. Equality Constraints and Lagrange Multipliers	7
1.4. Methods of Mathematical Programming	11
1.5. Iterative Search Methods	13
1.6. On Some Stochastic Optimization Techniques	17
Chapter 2: Dynamic optimization problems	45
2.1. Discrete Representations and Dynamic Programming Algorithms	45
2.2. Recurrence Equations	47
2.3. Discrete Processes Linear with Respect to the Time Interval	51
2.4. Discrete Algorithm of the Pontryagin's Type for Processes Linear in θ^N	55
2.5. Hamilton–Jacobi–Bellman Equations for Continuous Systems	58
2.6. Continuous Maximum Principle	70
2.7. Calculus of Variations	73
2.8. Viscosity Solutions and Nonsmooth Analyses	76
2.9. Stochastic Control and Stochastic Maximum Principle	84
Chapter 3: Energy limits for thermal engines and heat pumps at steady states	85
3.1. Introduction: Role of Optimization in Determining Thermodynamic Limits	85
3.2. Classical Problem of Thermal Engine Driven by Heat Flux	90
3.3. Toward Work Limits in Sequential Systems	108
3.4. Energy Utilization and Heat Pumps	111
3.5. Thermal Separation Processes	115
3.6. Steady Chemical, Electrochemical, and Other Systems	117
3.7. Limits in Living Systems	122
3.8. Final Remarks	123
Chapter 4: Hamiltonian optimization of imperfect cascades	127
4.1. Basic Properties of Irreversible Cascade Operations with a Work Flux	127

4.2.	Description of Imperfect Units in Terms of Carnot Temperature Control	132
4.3.	Single-Stage Formulae in a Model of Cascade Operation	138
4.4.	Work Optimization in Cascade by Discrete Maximum Principle	141
4.5.	Example	155
4.6.	Continuous Imperfect System with Two Finite Reservoirs	157
4.7.	Final Remarks	164
Chapter 5:	Maximum power from solar energy	167
5.1.	Introducing Carnot Controls for Modeling Solar-Assisted Operations	167
5.2.	Thermodynamics of Radiation	175
5.3.	Classical Exergy of Radiation	180
5.4.	Flux of Classical Exergy	184
5.5.	Efficiencies of Energy Conversion	186
5.6.	Towards a Dissipative Exergy of Radiation at Flow	187
5.7.	Basic Analytical Formulae of Steady Pseudo-Newtonian Model	190
5.8.	Steady Nonlinear Models applying Stefan–Boltzmann Equation	192
5.9.	Dynamical Theory for Pseudo-Newtonian Models	195
5.10.	Dynamical Models using the Stefan–Boltzmann Equation	204
5.11.	Toward the Hamilton–Jacobi–Bellman Approaches	211
5.12.	Final Remarks	212
Chapter 6:	Hamilton–Jacobi–Bellman theory of energy systems	215
6.1.	Introduction	215
6.2.	Dynamic Optimization of Power in a Finite-Resource Process	216
6.3.	Two Different Works and Finite-Rate Exergies	219
6.4.	Some Aspects of Classical Analytical HJB Theory for Continuous Systems	223
6.5.	HJB Equations for Nonlinear Power Generation Systems	225
6.6.	Analytical Solutions in Systems with Linear Kinetics	227
6.7.	Extensions for Systems with Nonlinear Kinetics and Internal Dissipation	230
6.8.	Generalized Exergies for Nonlinear Systems with Minimum Dissipation	232
6.9.	Final Remarks	235
Chapter 7:	Numerical optimization in allocation, storage and recovery of thermal energy and resources	237
7.1.	Introduction	237
7.2.	A Discrete Model for a Nonlinear Problem of Maximum Power from Radiation	239

7.3.	Nonconstant Hamiltonians and Convergence of Discrete DP Algorithms to Viscosity Solutions of HJB Equations	240
7.4.	Dynamic Programming Equation for Maximum Power From Radiation	249
7.5.	Discrete Approximations and Time Adjoint as a Lagrange Multiplier	250
7.6.	Mean and Local Intensities in Discrete Processes	257
7.7.	Legendre Transform and Original Work Function	259
7.8.	Numerical Approaches Applying Dynamic Programming	261
7.9.	Dimensionality Reduction in Dynamic Programming Algorithms	265
7.10.	Concluding Remarks	267
Chapter 8:	Optimal control of separation processes	271
8.1.	General Thermokinetic Issues	271
8.2.	Thermodynamic Balances Toward Minimum Heat or Work	273
8.3.	Results for Irreversible Separations Driven by Work or Heat	279
8.4.	Thermoeconomic Optimization of Thermal Drying with Fluidizing Solids	282
8.5.	Solar Energy Application to Work-Assisted Drying	312
8.6.	Concluding Remarks	320
Chapter 9:	Optimal decisions for chemical reactors	321
9.1.	Introduction	321
9.2.	Driving Forces in Transport Processes and Chemical Reactions	321
9.3.	General Nonlinear Equations of Macrokinetics	323
9.4.	Classical Chemical and Electrochemical Kinetics	325
9.5.	Inclusion of Nonlinear Transport Phenomena	326
9.6.	Continuous Description of Chemical (Electrochemical) Kinetics and Transport Phenomena	329
9.7.	Toward Power Production in Chemical Systems	330
9.8.	Thermodynamics of Power Generation in Nonisothermal Chemical Engines	334
9.9.	Nonisothermal Engines in Terms of Carnot Variables	337
9.10.	Entropy Production in Steady Systems	339
9.11.	Dissipative Availabilities in Dynamical Systems	340
9.12.	Characteristics of Steady Isothermal Engines	342
9.13.	Sequential Models for Dynamic Power Generators	349
9.14.	A Computational Algorithm for Dynamical Process with Power Maximization	353
9.15.	Results of Computations	356
9.16.	Some Additional Comments	357
9.17.	Complex Chemical Power Systems with Internal Dissipation	357

Chapter 10:	Fuel cells and limiting performance of electrochemobiological systems	373
10.1.	Introduction	373
10.2.	Electrochemical Engines	373
10.3.	Thermodynamics of Entropy Production and Power Limits in Fuel Cells	379
10.4.	Calculation of Operational Voltage	383
10.5.	Thermodynamic Account of Current-Dependent and Current-Independent Imperfections	389
10.6.	Evaluation of Mass Flows, Power Output, and Efficiency	392
10.7.	Quality Characteristics and Feasibility Criteria	395
10.8.	Some Experimental Results	396
10.9.	Assessing Power Limits in Steady Thermoelectrochemical Engines	401
10.10.	Hybrid Systems	404
10.11.	Unsteady States, Dynamical Units, and Control Problems	407
10.12.	Biological Fuel Cells and Biological Sources of Hydrogen	413
10.13.	Energy and size Limits for Living Organisms in Biological Systems	415
10.14.	A Brief Commentary on Development and Evolution of Species	423
Chapter 11:	Systems theory in thermal and chemical engineering	429
11.1.	Introduction	429
11.2.	System Energy Analyses	430
11.3.	Mathematical Modeling of Industrial Energy Management	430
11.4.	Linear Model of the Energy Balance for an Industrial Plant and its Applications	433
11.5.	Nonlinear Mathematical Model of a Short-Term Balance of Industrial Energy System	437
11.6.	Mathematical Optimization Model for the Preliminary Design of Industrial Energy Systems	439
11.7.	Remarks on Diverse Methodologies and Link with Ecological Criteria	444
11.8.	Control Thermodynamics for Explicitly Dynamical Systems	450
11.9.	Interface of Energy Limits, Structure Design, Thermoeconomics, and Ecology	452
11.10.	Toward the Thermoeconomics and Integration of Heat Energy	463
Chapter 12:	Heat integration within process integration	465
Chapter 13:	Maximum heat recovery and its consequences for process system design	475
13.1.	Introduction and Problem Formulation	475
13.2.	Composite Curve (CC) Plot	477

13.3. Problem Table (PR-T) Method	484
13.4. Grand Composite Curve (GCC) Plot	488
13.5. Special Topics in MER/MUC Calculations	492
13.6. Summary and Further Reading	496
Chapter 14: Targeting and supertargeting in heat exchanger network design	499
14.1. Targeting Stage in Overall Design Process	499
14.2. Basis of Sequential Approaches for HEN Targeting	500
14.3. Basis of Simultaneous Approaches for HEN Targeting	505
Chapter 15: Minimum utility cost (MUC) target by optimization approaches	507
15.1. Introduction and MER Problem Solution by Mathematical Programming	507
15.2. MUC Problem Solution Methods	510
15.3. Dual Matches	523
15.4. Minimum Utility Cost Under Disturbances	526
Chapter 16: Minimum number of units (MNU) and minimum total surface area (MTA) targets	533
16.1. Introduction	533
16.2. Minimum Number of Matches (MNM) Target	534
16.3. Minimum Total Area for Matches (MTA-M) Target	553
16.4. Minimum Number of Shells (MNS) Target	559
16.5. Minimum Total Area for Shells (MTA-S) Target	563
Chapter 17: Simultaneous HEN targeting for total annual cost	571
Chapter 18: Heat exchanger network synthesis	585
18.1. Introduction	585
18.2. Sequential Approaches	586
18.3. Simultaneous Approaches to HEN Synthesis	604
Chapter 19: Heat exchanger network retrofit	621
19.1. Introduction	621
19.2. Network Pinch Method	624
19.3. Simultaneous Approaches for HEN Retrofit	634
Chapter 20: Approaches to water network design	651
20.1. Introduction	651
20.2. Mathematical Models and Data for Water Network Problem	655
20.3. Overview of Approaches in the Literature	659
References	697
Glossary of symbols	773
Index	783