SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA
FACULTY OF CHEMICAL AND FOOD TECHNOLOGY

Reference number: FCHPT-19990-22507

OPTIMAL OPERATION OF BATCH MEMBRANE PROCESSES

DISSERTATION THESIS

Bratislava, 2012 Ing. Radoslav Paulen

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Study program: Process Control
Study field number: 2621
Study field: 5.2.14 Automation
Workplace: Department of Information Engineering and Process Control
Supervisor: Prof. Ing. Miroslav Fikar, DrSc.

Bratislava, 2012 **Ing. Radoslav Paulen**

Acknowledgements

There are several people I have met throughout my doctoral studies who really helped me in many ways, took me in a lot of discussions (some of which were scientific ones), and contributed to the level of my understanding of the world of chemical and process engineering. This is the place where these people are mentioned to give them at least a bit of credit for their guidance, support, kindness, and friendship.

I would like to express my sincere gratitude to my supervisor professor Miroslav Fikar for his patient guidance, for lot of inspiration I have received from him from my early studies at Slovak University of Technology (STU) in Bratislava and for supporting me in all possible ways, to professor Abderrazak Latifi for giving me the opportunity to become a part of his group at Ecole Nationale Supérieure des Industries Chimiques (ENSIC) at INPL in Nancy for more than one year in sum, to doctor Benoît Chachuat for being my supervisor during my stay at Imperial College London, and to professor Sigurd Skogestad for warm welcome and hospitality during my stay in his group at NTNU in Trondheim. Professors Ján Mikleš, Ján Dvoran, Alojz Mészáros, Monika Bakošová, Michal Kvasnica, Anna Kolesárová, and Vladimír Baláž from the Institute of Information Engineering, Automation, and Mathematics (IAM) at STU in Bratislava and professors Boris Rohál-Il'kiv, Ivan Taufer, Jozef Markoš, Štefan Schlosser, François Lesage, Micheal Daroux, Jean-Pierre Corriou, Tor Arne Johansen, and Greg Foley are also among those I want to mention in order to thank them for their unreserved aid whenever I needed it.

Following document presents already a revised version of my dissertation thesis. It is revised based on the comments I received from the reviewers of the thesis, professors Alena Kozáková and Antonín Víteček, whom I am greatly indebted. At this place, I would also like to thank to Mario E. Villanueva and Martin Jelemenský for proofreading.

There are few other people at IAM I would like to thank to: Andrea Kalmárová, Katarína Macušková, and Monika Mojžišová for being helpful in processing paper and administrative works, Michal Čižniar for introducing me into the world of optimization, Martin Herceg, Ivana Rauová, and Richard Valo for being the best officemates man can have, and Stano Vagač, Ľuboš Čirka, Katarína Matejíčková, Jana Závacká, Lenka Blahová, Marian Podmajerský, Martin Kalúz, Jana Kmeťová, Juraj Oravec and Alexander Szűcs for everything.

Special thanks are devoted to my friend, doctor Zoltán Kovács, who introduced me to the world of membrane filtration. Henrik Manum, Johanes Jäschke, Magnus Jacobsen, Ramprasad Yelchuru, Brahim Benyahia, Shahid Ayoub, Stephane Quino, Ahmed Maidi, Ali Assaf, Salim Zodi, Amine Bouarab, Huan Dinh Nguyen, Dinh Nang Le, Aziz Assad, Billy Homeky, Juan Lizardo, Ivan Gil, Minghai Lei, Lei Wang, Mylène Detchebbery, Martin Jelemenský, Lívia Petáková, Mario E. Villanueva, Jai Rajyaguru, Channarong "K" Puchongkawarin, Boris Houska, Andreas Nikolaou, and Cheng S. Khor are the last people mentioned for whom I am indebted for making my abroad research stays pleasant and inspirational.

Last but the biggest "Thank You!" is devoted to members of my family who are here for me and stand behind me whenever I need.

Radoslav Paulen
Bratislava, 2012

Abstract

This work considers the problem of finding the optimal control of batch membrane diafiltration processes. Diafiltration is known as an effective method to separate at least two solutes from given solution (liquor) at the base of their different molecular (particle) effective sizes. The goal is to concentrate (increase the concentration of) the solute(s) with bigger particle size(s) usually called macro-solute and to remove impurities, i.e. to dilute (decrease the concentration of) solute(s) with smaller particle size(s) traditionally denoted as micro-solute. The whole process is described by the set of ordinary differential equations and thus methods of dynamic optimization (open-loop optimal control) can be used to establish optimal operation of these processes.

Our task is to determine how a solute-free solvent (diluant) should be dynamically added to feed solution tank throughout the process run to achieve given separation goal in minimum time or with minimum amount of added diluant. We use analytical approach, Pontryagin's Minimum Principle, to identify candidates for optimal control taking into account the necessary conditions for optimality. Based on these, we derive optimal operational policies for batch membrane processes of several types. Direct (discrete) numerical method of dynamic optimization, Control Vector Parameterization, is then used to confirm the theoretical findings and to obtain the optimal diluant utilization for particular process and instance.

Keywords: Optimal Control, Dynamic Optimization, Membrane Filtration, Pontryagin's Minimum Principle, Control Vector Parameterization, Diafiltration

Abstrakt

Táto práca sa zaoberá problémom nájdenia optimálneho riadenia vsádzkových membránových diafiltračných procesov. Diafiltrácia je známa ako efektívna metóda separácie najmenej dvoch rozpustených zložiek danej zmesi (roztoku) na základe rozdielnej účinnej veľkosti ich častíc. Jej cieľom je koncentrovať rozpustené zložky s väčšou veľkosťou častíc a odstrániť nečistoty, teda znížiť koncentráciu rozpustených zložiek s menšou veľkosťou častíc. Celý proces je opísaný súborom obyčajných diferenciálnych rovníc a teda je možné použiť metódy dynamickej optimalizácie na určenie optimálneho riadenia týchto procesov. Našim cieľom je určiť ako by malo byť do nádrže s roztokom v závislosti od času pridávané rozpúšťadlo, počas behu samotného procesu, tak, aby sa dosiahlo splnenie požadovaného separačného zámeru v minimálnom čase alebo s použitím minimálneho množstva pridávaného rozpúšťadla. Použitím analytického prístupu, Pontrjaginovho princípu minima, identifikujeme kandidátov pre optimálne riadenie berúc do úvahy nevyhnutné podmienky optimality. Na základe týchto odvodíme optimálnu réžiu pre vsádzkové membránové procesy viacerých typov. Následne je použitá priama (diskrétna) metóda dynamickej optimalizácie, Parametrizácia vektora riadenia, ktorá potvrdí teoretické zistenia a pomocou ktorej získame optimálne použitie rozpúšťadla pre konrétny proces a zadanie úlohy optimálneho riadenia.

Kľúčové slová: Optimálne riadenie, Dynamická optimalizácia, Membránová filtrácia, Pontrjaginov princíp minima, Parametrizácia vektora riadenia, Diafiltrácia

Contents

List of Figures

List of Tables

List of Abbreviations

AV	Adjoint Variables
BB	Branch–and–Bound
BCI	Boundary Condition Iteration
C	Concentration (mode)
CVD	Constant-Volume Diafiltration
CVI	Control Vector Iteration
CVP	Control Vector Parametrization
DF	Diafiltration
D	Dilution (mode)
DO	Dynamic Optimization
DVD	Dynamic-Volume Diafiltration
FD	Finite Differences
IP	Interior Point
IVP	Initial Value Problem
MF	Microfiltration
NCO	Necessary Conditions for Optimality
NF	Nanofiltration

NLP	Non Linear Programming
ODE	Ordinary Differential Equation
OC	Orthogonal Collocation
OCP	Optimal Control Problem
PWC	Piece-wise Constant
RO	Reverse Osmosis
SE	Sensitivity Equations
SQP	Sequential Quadratic Programming
TPBVP	Two-point Boundary Value Problem
UF	Ultrafiltration
VVD	Variable-Volume Diafiltration
VCF	Volume Concentration Factor

Nomenclature

ΔP	transmembrane pressure
$\hat{\boldsymbol{u}}(t)$	vector of polynomial approximations of control variables
$\hat{\boldsymbol{x}}(t)$	vector of polynomial approximations of state variables
$\mathbf{0}$	all-zeros vector
$\mathbf{1}$	all-ones vector
$\mathbf{Q}$	state weighting matrix of dimension $n_x \times n_x$
$\mathbf{R}$	control weighting matrix of dimension $n_u \times n_u$
$\mathcal{J}^\star$	value function, cost-to-go
$\mathcal{F}(\cdot)$	integrand in objective functional
$\mathcal{G}(\cdot)$	non-integral part of objective functional
$\mathcal{J}$	objective functional
$\boldsymbol{p}$	vector of parameters
$\boldsymbol{u}(t)$	vector of control variables
$\boldsymbol{x}(t)$	vector of state variables

$\boldsymbol{y}$ vector of optimized parameters

c concentration

H Hamiltonian function

k mass transfer coefficient

n_p dimension of the vector of parameters

n_u dimension of the vector of state variables

n_x dimension of the vector of state variables

q flux, flow through the membrane

R rejection coefficient

R_m membrane resistance

S singular state surface

t independent time variable

$u(t)$ flowrate of pure diluant into the feed tank

V feed tank volume

z exponent in the wall correction factor in Eq. (6.8)

Greek Symbols

α control variable of diafiltration process

γ numerical parameter in (3.31), coefficient in Eq. (6.8)

μ viscosity

π osmotic pressure

$\boldsymbol{\lambda}$ vector of adjoint variables

Mathematical Notation

$\mathbb{A}$	vector space, set
$\mathbb{R}$	real-vector space
$\mathbb{S}$	space of symmetric matrices
$\mathbf{A}$	matrix
$\mathcal{A}$	functional
$\boldsymbol{a}$	vector or vector function
a, A	scalar or scalar function

Subscripts

0	initial
sing	singular
f	final
max	maximal value, upper bound
min	minimal value, lower bound
1	macro-solute
2	micro-solute
g	gel
lim	limiting
p	permeate
w	wall

Chapter 1

Introduction

"See first, think later, then test. But always see first. Otherwise you will only see what you were expecting."
Douglas Adams (1952 - 2001)

Principles of optimality govern our everyday life. Any natural or artificial system, which surrounds us or influences our closest vicinity, tends to operate optimally, i.e. it tries to maximize or minimize some given function under present constraints. This can be seen even in such microscopic phenomena as bonding of atoms to form molecules in order to minimize the overall potential energy (function). Neural network in human body uses minimum wiring material (neuron connections) under constraint of amount of transfered information. Seeds in flower of sunflower are collocated in order to maximize their number subject to the given area and the seed shape. In these cases, it is nature which decided, using evolutionary (trial and error, survival of the fittest) principle, about optimal design of such systems.

Artificial systems, such as traffic, electricity, or logistic networks, are designed by engineers who express the objective and constraints in mathematical form of functions and equations. Using such mathematical model of the reality, actual design problem can be then solved by exploiting tools (e.g. algorithms) provided by mathematics and computer science. Solution is then given by a set of discrete values of decision (optimization) variables. Once this is done, we are sure that nothing better is possible to achieve for the actual form of objective and constraint functions and for the actual state of the system.

But what if system state or any of these functions involved in optimization problem are changing over the time? Then, we obviously need to repeat the whole optimal design procedure at each time instant. From practical point of view, we no longer speak about discrete decision (control) actions but we consider the corresponding time-dependent trajectories. We attribute all dynamic changes happening at observed system to an entity which we call process. Again, since our goal is the optimization of the system, we need to come up with mathematical model of the reality, dynamic (process) model.

It is interesting to note that a variety of problems of design of optimal process operation (i.e. optimal process control) problems arises in fields of engineering (chemical, mechanical, optical, ...), computer science, economics, finance, operations research and management science, astronomy, physics, structural and molecular biology, medicine, and material science. Such problems include finding of optimal control strategy which minimizes energy or raw material consumptions during the production processes, maximizes production profit, or leads to optimal process model identification (optimal experiment design, parameter estimation). Even that similar concepts from static design apply for this optimization problem, the situation is slightly complicated by the presence of dynamic forms of system state and objective and constraint functions.

Tools for solving static optimal design problem are dated back to the end of first half of the last century. Development of linear programing methods, followed soon by non-linear programming (NLP) ones, enabled for effective computer solving of various engineering problems arising in many fields. Dynamic optimization represents a mathematical approach for solving problems of open-loop optimal process control. In principle, there are two different approaches in effort to solve DO problems, namely deterministic and stochastic ones. In this work we investigate only deterministic approaches; for stochastic approaches (those which simulate decision processes of nature) see Chang (2004); Fleming and Rishel (1975).

The techniques utilized to solve DO problems in class of deterministic approaches fall under two broad frameworks: variational (indirect) methods and discretization (direct) methods. Variational methods address the DO problem in its original infinite–dimensional form exploiting the classical calculus of variations together with dynamic programming or Pontryagin's maximum/minimum principle (Pontryagin et al., 1962). A big advantage of this is that we are looking for an exact solution to problem without any transformations. On the other hand, use of these approaches can get difficult if we want to solve DO

problem for not quite simple systems. Then a discretization plays important role since original infinite dimensional problem is transformed to a non-linear programing problem. Once transformed into static form, DO problem can be solved approximatively by means of static optimization just like in static optimal design. It is then only a matter of utilized degree and form of discretization how close will obtained solution be to the original problem. Discretization methods can be subdivided into two broad classifications known as simultaneous and sequential.

The simultaneous method is a complete discretization of both state and control variables often achieved via collocation (Tsang et al., 1975). While completely transforming a dynamic system into a system of algebraic equations eliminates the problem of optimizing in an infinite dimensional space, simultaneous discretization has the unfortunate side effect of generating a multitude of additional variables yielding large, unwieldy NLPs that are often impractical to solve numerically.

Sequential discretization, usually achieved via control parameterization (Brusch and Schappelle, 1973), is a discretization approach in which the control variable profiles are approximated by a sum of basis functions in terms of a finite set of real parameters. These parameters then become the decision variables in a dynamic embedded NLP. Function (functional) evaluations are provided to this NLP via numerical solution of a fully determined initial value problem (IVP), which is given by fixing the control profiles. This method has the advantages of yielding a relatively small NLP and exploiting the robustness and efficiency of modern IVP and sensitivity solvers (Chachuat et al., 2006).

In this work, we deal with membrane processes which stand for an emerging technology in chemical and bioprocess industry used both in production and down-stream processing. Membrane processes, such as membrane distillation, pervaporation, membrane purification, diafiltration and processes exploiting membrane-equipped reactors, are receiving growing attention mainly due to reduced energy demands and higher efficiency of the achieved separation or processing goals. These systems, however, did not receive much attention from process optimization community and that is why they provide many opportunities e.g. for development of optimal operation design.

Despite that literature on optimal control of membrane processes is not very rich, various dynamic optimization problems were already solved. These applications include optimization of membrane reactors performance (Parvasi et al., 2009; Rahimpour and Behjati, 2009), other membrane-assisted processes (Bui et al., 2010; Kuhn et al., 2009), membrane

separation (Fikar et al., 2010) as well as membrane fouling and cleaning (Blankert et al., 2006; Boxtel and Otten, 1993; Zondervan and Roffel, 2008). This study concentrates on finding of general optimal operation of batch diafiltration processes which are a particular class of membrane separation/purification processes.

Purification of solution can be achieved by employing semi-permeable membrane which retains or concentrates (in)valuable species. Diafiltration process combines two possible ways of how to treat a solution to concentrate its valuable components and to dilute (dispose off) present impurities. It can be performed continuously or discontinuously. This depends on several physical factors and on properties of initial solution as well as final product. This process can be controlled, either in continuous or batch setup, by influencing concentrations by using of solute-free solvent (diluant). Utilization of this diafiltration buffer can be dynamically adjusted to optimize the process performance, e.g. minimum time or minimum diluant operation can be reached.

This work is organized as follows. First part introduces theory of optimal control, DO, and membrane processes in a way to provide tools which are exploited in the second part for finding of optimal operation of batch diafiltration processes. The theory involves introduction to problems of dynamic optimization mainly from an chemical engineering point of view. It is followed by explanation of methods (analytical and numerical ones) which can be exploited to treat problems of optimal control of membrane processes introduced in the last section of theoretical part.

Implementation and advanced utilization of numerical methods of dynamic optimization were published in:

- Paulen, R. – Fikar, M. – Čižniar, M. – Latifi, M. A.: Global Optimization for Parameter Estimation of Dynamic Systems. AT&P Journal Plus, no. 2, pp. 71-78, 2009.

- Paulen, R. – Fikar, M. – Latifi, M. A.: Dynamic Optimization of a Polymerization Reactor. In 18th Mediterranean Conference on Control and Automation, Marrakech, Morocco, pp. 733-738, 2010.

- Paulen, R. – Fikar, M.: Tighter Convex Relaxations for Global Optimization Using alphaBB Based Approach. Editor(s): Fikar, M., Kvasnica. M., In Proceedings of the 18th International Conference on Process Control, Slovak University of Technology in Bratislava, Tatranská Lomnica, Slovakia, pp. 537-542, 2011.

Second part then builds upon the theoretical basis and uses it to establish solution to treated problems. Finally, multiple case studies are shown in order to present various aspects of considered optimal control problems and to discuss possible advantages and drawbacks of real implementation of optimal operation of diafiltration processes.

Numerical as well as analytical ways of finding an optimal control of diafiltration processes were showed in:

- Paulen, R. – Fikar, M. – Kovács, Z. – Czermak, P.: Optimal Control of Diafiltration Process for Albumin Production. In Preprints of the 18th IFAC World Congress Milano (Italy) August 28 – September 2, 2011, pp. 14007-14012, 2011.
- Paulen, R. – Fikar, M. – Kovács, Z. – Czermak, P.: Process optimization of diafiltration with time-dependent water adding for albumin production. Chemical Engineering and Processing: Process Intensification, no. 8, vol. 50, pp. 815-821, 2011.
- Paulen, R. – Fikar, M. – Foley, G. – Kovács, Z. – Czermak, P.: Time-optimal diafiltration under gel polarization conditions. In ICOM 2011 - Book of abstracts, pp. 379-380, 2011.
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- Paulen, R. – Fikar, M. – Foley, G. – Kovács, Z. – Czermak, P.: Time-Optimal Batch Diafiltration, In IFAC Symposium on Advanced Control of Chemical Processes ADCHEM 2012, Singapore, *accepted*.
- Paulen, R. – Fikar, M. – Foley, G. – Kovács, Z. – Czermak, P.: Optimal feeding strategy of diafiltration buffer in batch membrane processes, Journal of Membrane Science, vol 411-412, pp. 160-172, 2012.

Goals of the Thesis

The main aim of this thesis is to study dynamic optimization and control of batch diafiltration processes, to explore the existing operation practice, and to provide improved operation based on the optimal control theory.

In detail, the objectives can be summarized as follows:

- Study of optimal control for general diafiltration processes
- Derivation of analytical solution for most common class of batch diafiltration processes
- Proposition of a simple numerical approach to treat the general case of optimal operation finding for batch diafiltration processes
- Comparison the resulting optimal operation with the standard control techniques and giving insightful discussion of advantages of optimal operation and of future challenges for optimal operation of diafiltration processes

Part I

Theory

Chapter 2

Optimal Control Problem

Optimal control of any process can be achieved either in open or closed loop. In this work we concentrate far more on the first class. However, the same optimality principles mentioned apply analogously for the closed-loop schemes as well. This chapter is devoted to definition of open-loop optimal control (dynamic optimization) problems. Next chapter is then concerned with practical ways (techniques) which can be used to solve such problems.

We introduce three basic parts of the optimal control problem (OCP): objective functional, constraint functions, and process model and their common mathematical forms. Objective functional, optimization criterion, or performance index represents mathematical expression of phenomenon which minimum (or maximum) we want to attain. The constraint functions of various types determine a search space of decision (optimization) variables which time evolutions or values are searched for. Process model function ties inputs, states and outputs of the process together and determines a search domain for optimization procedure in a similar way the constraint functions do.

2.1 Objective Functional

Objective functional expresses costs or benefits of a process which one wants to either avoid or reach. Dynamic optimization objective functional can be in general defined in three different forms which can be converted easily one to another (Kirk, 1970). Mathematical representation of these form follows together with the year of approximate first appearance in the literature.

Lagrange form (1780)

$$\mathcal{J} = \int_{t_0}^{t_\mathrm{f}} \mathcal{F}\left(\boldsymbol{x}(t), \boldsymbol{u}(t), \boldsymbol{p}, t\right) \mathrm{d}t, \tag{2.1a}$$

Mayer form (1890)

$$\mathcal{J} = \mathcal{G}\left(\boldsymbol{x}(t_\mathrm{f}), \boldsymbol{p}, t_\mathrm{f}\right), \tag{2.1b}$$

Bolza form (1900)

$$\mathcal{J} = \mathcal{G}\left(\boldsymbol{x}(t_\mathrm{f}), \boldsymbol{p}, t_\mathrm{f}\right) + \int_{t_0}^{t_\mathrm{f}} \mathcal{F}\left(\boldsymbol{x}(t), \boldsymbol{u}(t), \boldsymbol{p}, t\right) \mathrm{d}t. \tag{2.1c}$$

Here t represents independent time variable, indices $\square_0$ and $\square_\mathrm{f}$ indicate initial and final process state respectively, $\boldsymbol{x}(t) \in \mathbb{R}^{n_x}$ is a vector of state variables, $\boldsymbol{u}(t) \in \mathbb{R}^{n_u}$ denotes a vector of control variables which are going to be optimized[1]. Time independent decision variables, traditionally called parameters, are denoted by $\boldsymbol{p} \in \mathbb{R}^{n_p}$. $\mathcal{J}$, $\mathcal{G}(\cdot)$ and $\mathcal{F}(\cdot)$ are then real-valued functions (functionals) since $\mathcal{G} : \mathbb{R}^{n_x} \times \mathbb{R}^{n_p} \times \mathbb{R} \to \mathbb{R}$ and $\mathcal{F} : \mathbb{R}^{n_x} \times \mathbb{R}^{n_u} \times \mathbb{R}^{n_p} \times [t_0, t_\mathrm{f}] \to \mathbb{R}$.

2.1.1 Typical Optimal Control Tasks

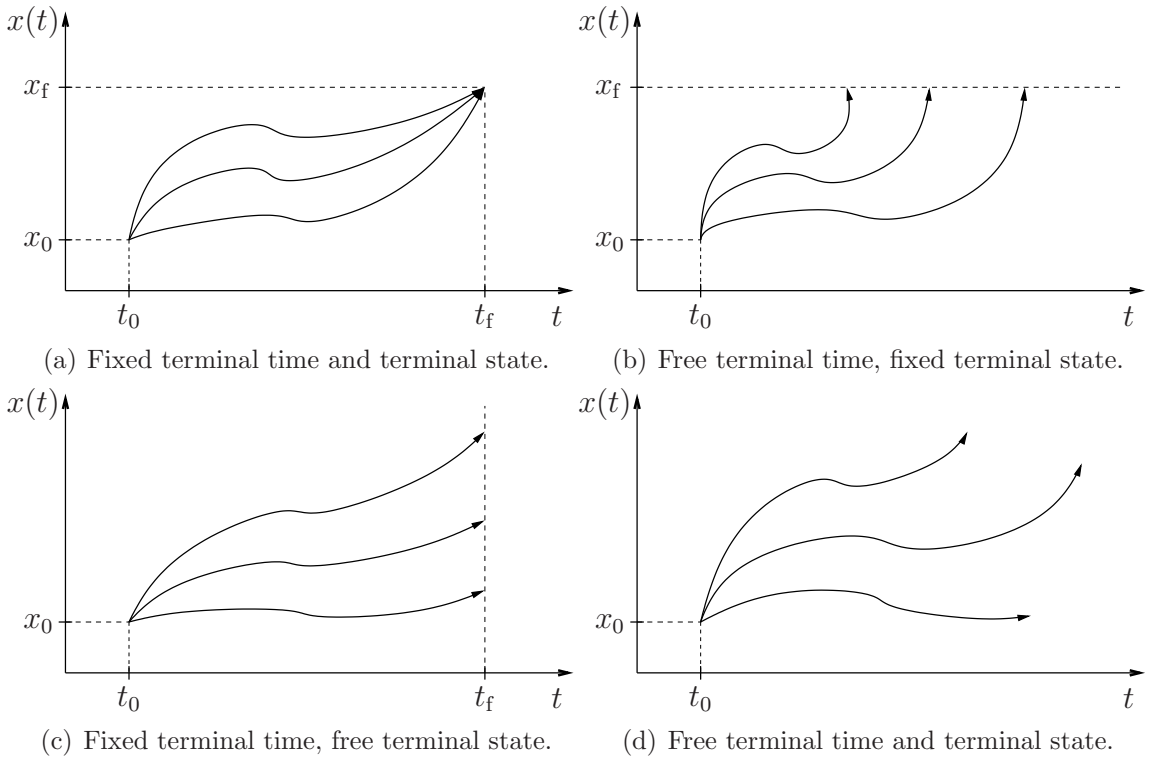
One chooses an approach of solving OCP based on the type (structure) of this problem. There are several types of optimal control tasks which are distinguished e.g. by fixed/free initial/terminal time/state. Initial time is usually fixed since it is either the time when we start to observe the process or the time when some previous process (which duration may have been optimized) ends. Many applications consider initial state to be a free parameter which is chosen such that designed process is optimal. However this is omitted in Fig. 2.1 where we show schematic representation of the most common optimal control tasks.

Using different forms of objective functionals one can consider different control problems. Historically the first form of functional, Lagrange form, can be used, according to mathematical form of $\mathcal{F}(\cdot)$ in (2.1a), for the following ones:

(i) Minimum control effort problem

$$\mathcal{F} \equiv \|\boldsymbol{u}\|. \tag{2.2a}$$

[1]Explicit time-dependency of state and control variables will be usually omitted in this study for the purpose of better readability of the text. Hence it holds that $\boldsymbol{x}(t) \equiv \boldsymbol{x}$ and $\boldsymbol{u}(t) \equiv \boldsymbol{u}$.



(a) Fixed terminal time and terminal state.

(b) Free terminal time, fixed terminal state.

(c) Fixed terminal time, free terminal state.

(d) Free terminal time and terminal state.

Figure 2.1: Typical optimal control tasks.

With $\|\cdot\|$ being appropriate norm, this form of functional represents an approach of direct minimization of process expenses since the goal is to minimize control effort (e.g. energy) needed for transfer state $\boldsymbol{x}(t)$ from specified point $\boldsymbol{x}_0$ to required $\boldsymbol{x}_\mathrm{f}$ in given or unspecified time t_f. This is visualized in Fig. 2.1(a) and 2.1(b).

(ii) Minimum time problem

$$\mathcal{F} \equiv 1. \tag{2.2b}$$

represents historically the first optimal control problem treated (brachistochrone problem proposed by Johan Bernoulli). For the optimization of chemical processes, use of this functional is one possibility of how indirectly (but globally) minimize operational process expenses such as electricity needed to power the pumps and heaters, amount of heating and cooling media used and so on. This problem is to find such control which drive process from given initial state $\boldsymbol{x}_0$ to prescribed (fixed) final state $\boldsymbol{x}_\mathrm{f}$ in minimum time possible. This can be schematically represented by Fig. 2.1(b) as finding of time-optimal transition trajectory between $\boldsymbol{x}_0$ and $\boldsymbol{x}_\mathrm{f}$.

(iii) LQ (linear-quadratic) problem

$$\mathcal{F} \equiv \frac{1}{2}(\boldsymbol{x}^T\mathbf{Q}\boldsymbol{x} + \boldsymbol{u}^T\mathbf{R}\boldsymbol{u}). \tag{2.2c}$$

This problem considers linear process model (to be defined later herein) and quadratic criterion such that $\mathbf{Q} \in \mathbb{S}^{n_x}$ and $\mathbf{R} \in \mathbb{S}^{n_u}$ are symmetric positive semi-definite and positive definite matrices respectively which weight the steering from point $\boldsymbol{x}_0$ to point as close as possible to the origin (zero) and the control used for this task. Terminal time is usually specified for this kind of problem and it is then desired to choose one of the admissible state trajectories (shown in Fig. 2.1(c)) which minimizes the functional. This type of functional is often used in closed-loop optimal control since it yields Lyapunov function which properties guarantee the stability of closed-loop control system.

Mayer form allows for optimization of some final point criterion and can used as a criterion for many optimal control tasks.

(i) Minimum time problem

$$\mathcal{G} \equiv t_\mathrm{f}. \tag{2.3a}$$

This represents the very same problem as discussed before (2.2b) and thus an example of how considered functional forms are closely connected and interchangeable. Indeed, the correct approach of interchanging those forms is to provide an additional ODE such as $\dot{x}_{n_x+1} = 1$ and to state the criterion in Mayer form as $\mathcal{G} \equiv x_{n_x+1}(t_\mathrm{f})$ which equivalent to (2.3a).

(ii) Terminal control problem

$$\mathcal{G} \equiv \|\boldsymbol{x}(t_\mathrm{f}) - \boldsymbol{x}_\mathrm{f}\|. \tag{2.3b}$$

This form of functional represents direct expression of goals of the process itself which are to be maximized or minimized. If speaking about chemical processes, this might represent minimization of the difference between desired and achieved purity or quantity of product or the same on the side of some unwanted by-products. Graphically this OCP can be represented by Figs. 2.1(c) and 2.1(d).

Bolza form of objective functional combines Lagrange and Mayer form and thus stands for the most general form. It is considered in our further discussions on optimal control since it comprises all possible objective functional forms.

2.2 Constraints

As stated above, constraint functions determine the optimization search space and can take various forms in general. Different equality and inequality constraints may be considered to bound the values of decision as well as state variables to respect safety or environmental safeguards, to state certain setpoints in control loop, and so on. Following list covers all types of considered constraints:

(i) Infinite dimensional equality constraint

$$h(\boldsymbol{x}, \boldsymbol{u}, \boldsymbol{p}, t) = 0, \qquad \forall t \in [t_{c,0}, t_{c,\mathrm{f}}],\ [t_{c,0}, t_{c,\mathrm{f}}] \subseteq [t_0, t_{\mathrm{f}}], \tag{2.4a}$$

is typically present in chemical processes. An example of using such kind of constraints is gas mixture separation where sum of mole fractions of all components, $\mathbf{1}^T\boldsymbol{x}$, must be equal to one at each time instance of the process.

(ii) Infinite dimensional inequality constraint

$$g(\boldsymbol{x}, \boldsymbol{u}, \boldsymbol{p}, t) \leq 0, \qquad \forall t \in [t_{c,0}, t_{c,\mathrm{f}}],\ [t_{c,0}, t_{c,\mathrm{f}}] \subseteq [t_0, t_{\mathrm{f}}], \tag{2.4b}$$

is also of great practical interest since it may express a limit of some resource which may not be overrun. Traditionally such kind of constraints is present as of so-called *box constraints* of a form $\boldsymbol{x} \in [\boldsymbol{x}_{\min}, \boldsymbol{x}_{\max}]$, where $\boldsymbol{x}_{\min}$ and $\boldsymbol{x}_{\max}$ denote lower and upper bounds on $\boldsymbol{x}$ respectively.

(iii) Point equality constraint

$$h(\boldsymbol{x}, \boldsymbol{u}, \boldsymbol{p}, t_c) = 0, \quad t_c \in [t_0, t_{\mathrm{f}}], \tag{2.4c}$$

is used to determine specific value (set of values) state/decision variables at distinct time points. This constraint is commonly used when we solve fixed terminal point problem, e.g. concentration of product is restricted to some value at the end of the reaction.

(iv) Point inequality constraint

$$g(\boldsymbol{x}, \boldsymbol{u}, \boldsymbol{p}, t_c) \leq 0, \quad t_c \in [t_0, t_{\mathrm{f}}], \tag{2.4d}$$

may be used in a similar way as the previous type, to ensure that some quantity does not exceed the specified limit at some distinct time point. For example, we may express required purity of the product of separation by this kind of constraint.

We note that all of these constraints can be expressed in the standard canonical form, an equivalent to the functional form (2.1c)

$$\mathcal{J}_c = \mathcal{G}_c\left(\boldsymbol{x}(t_c), \boldsymbol{p}, t_c\right) + \int_{t_{c,0}}^{t_{c,\mathrm{f}}} \mathcal{F}_c\left(\boldsymbol{x}, \boldsymbol{u}, \boldsymbol{p}, t\right) \mathrm{d}t, \tag{2.5}$$

where $c = 1, \ldots, n_c$ and n_c is the number of constraints. Constraints (2.4) can be rewritten into the canonical form such that for:

(i) Infinite dimensional equality constraint

$$\mathcal{G}_c = 0, \qquad \mathcal{F}_c = \omega\left(h(\boldsymbol{x}, \boldsymbol{u}, \boldsymbol{p}, t)\right)^2, \qquad \mathcal{J}_c = 0. \tag{2.6a}$$

where ω is zero if t runs outside the interval $[t_{c,0}, t_{c,f}]$. Otherwise it is an empirical positive and adjustable weighting factor which is used to improve the numerical accuracy.

(ii) Infinite dimensional inequality constraint

$$\mathcal{G}_c = 0, \qquad \mathcal{F}_c = \omega \max\left(0, g(\boldsymbol{x}, \boldsymbol{u}, \boldsymbol{p}, t)\right), \qquad \mathcal{J}_c = 0, \tag{2.6b}$$

(iii) Point equality constraint

$$\mathcal{G}_c = h\left(\boldsymbol{x}, \boldsymbol{u}, \boldsymbol{p}, t_c\right), \qquad \mathcal{F}_c = 0, \qquad \mathcal{J}_c = 0, \tag{2.6c}$$

(iv) Point inequality constraint

$$\mathcal{G}_c = g\left(\boldsymbol{x}, \boldsymbol{u}, \boldsymbol{p}, t_c\right), \qquad \mathcal{F}_c = 0, \qquad \mathcal{J}_c \leq 0, \tag{2.6d}$$

These can be adjoined to the cost functional $\mathcal{J}$ by a vector of Lagrange multipliers $\boldsymbol{\nu} \in \mathbb{R}^{n_c}$ to form an augmented functional $\bar{\mathcal{J}}$

$$\bar{\mathcal{J}} = \mathcal{J} + \sum_{c=1}^{n_c} \nu_c \mathcal{J}_c. \tag{2.7}$$

Equivalently this functional can be written as

$$\bar{\mathcal{J}} = \bar{\mathcal{G}} + \int_{t_0}^{t_\mathrm{f}} \bar{\mathcal{F}} \, \mathrm{d}t. \tag{2.8}$$

with

$$\bar{\mathcal{G}} = \mathcal{G} + \sum_{c=1}^{n_c} \nu_c \mathcal{G}_c, \quad \text{and} \quad \bar{\mathcal{F}} = \mathcal{F} + \sum_{c=1}^{n_c} \nu_c \mathcal{F}_c. \tag{2.9}$$

2.3 Process Model

In principle, process model represents additional set of equality constraints since in general it consists of a set of algebraic, differential, and/or functional equations which, if satisfied, give input-output or inner mathematical description of phenomena taking place in observed system.

While we study dynamic optimization of processes running in continuous time, a continuous time-dependent (dynamical) models are involved. The simplest type of the model which will guarantee these properties is model described by a set of ordinary differential equations (ODEs)

$$\dot{\boldsymbol{x}} = \boldsymbol{f}\left(\boldsymbol{x}, \boldsymbol{u}, \boldsymbol{p}, t\right), \qquad \forall t \in [t_0, t_\mathrm{f}]. \tag{2.10a}$$

Here the vector function $\boldsymbol{f}(\cdot)$ is such that $\boldsymbol{f} : \mathbb{R}^{n_x} \times \mathbb{R}^{n_u} \times \mathbb{R}^{n_p} \times [t_0, t_\mathrm{f}] \to \mathbb{R}^{n_x}$. If the solution $\boldsymbol{x}(t)$ to (2.10a) additionally satisfies the initial condition

$$\boldsymbol{x}(t_0, \boldsymbol{p}) = \boldsymbol{x}_0(\boldsymbol{p}), \tag{2.10b}$$

where $\boldsymbol{x}_0(\cdot)$ is such that $\boldsymbol{x}_0 : \mathbb{R}^{n_p} \to \mathbb{R}^{n_x}$, it is a solution to initial value problem (IVP) defined by (2.10).

Hence that, equation (2.10a) is written in the form we classify as non-autonomous differential equation. However, majority of physical processes are described by autonomous ODEs in the following form

$$\dot{\boldsymbol{x}} = \boldsymbol{f}\left(\boldsymbol{x}, \boldsymbol{u}, \boldsymbol{p}\right), \qquad \forall t \in [t_0, t_\mathrm{f}]. \tag{2.11}$$

This means that dynamics of the process are affected just by dynamics of process states and inputs, and by parameters, not by the time itself. Simply spoken, for the distinct process state, an action (control) performed at time τ has the same effect as the same action carried out at time $\tau + \Delta\tau$ where $\Delta\tau$ is arbitrary.

It is often the case that the structure of process model affects the complexity of optimal control problem dramatically. This is why the particular type of process model may decide about the optimization strategy used for solving of OCP.

2.3.1 Linear Time-Invariant System

A common approach to represent linear time-invariant systems is the state-space form

$$\dot{\boldsymbol{x}} = \mathbf{A}\boldsymbol{x} + \mathbf{B}\boldsymbol{u}, \qquad \boldsymbol{x}(t_0) = \boldsymbol{x}_0, \tag{2.12}$$

with state matrix $\mathbf{A} \in \mathbb{R}^{n_x \times n_x}$ and input matrix $\mathbf{B} \in \mathbb{R}^{n_x \times n_u}$. Solution of such set of ODEs is usually easily found to be:

$$\boldsymbol{x}(t) = \mathrm{e}^{\mathbf{A}t}\boldsymbol{x}_0 + \int_{t_0}^{t} \mathrm{e}^{\mathbf{A}(t-\tau)}\mathbf{B}\boldsymbol{u}(\tau)\mathrm{d}\tau, \tag{2.13}$$

where matrix $\mathrm{e}^{\mathbf{A}t}$ is traditionally called fundamental matrix of a system. Existence of such explicit solution gives certain advantage and implies that it is somewhat easier to find optimal control of processes which can be modeled in stated manner. This is why these kinds of models are widely used for representing processes behavior in optimal, robust, or feedback control. Moreover, equation (2.12) yields a set of convex equality constraints and therefore, provided that other considered constraints (2.4) are convex and the objective functional is of the form (2.2) or (2.3), the resulting optimal control problem is convex. In general, it is easier to solve convex rather than non-convex problem.

2.3.2 Input Affine System

In this work, majority of the interest is devoted to systems of a form

$$\dot{\boldsymbol{x}} = \boldsymbol{a}(\boldsymbol{x}) + \mathbf{B}(\boldsymbol{x})\boldsymbol{u}, \qquad \boldsymbol{x}(t_0) = \boldsymbol{x}_0, \tag{2.14}$$

where $\boldsymbol{a}(\cdot)$ and $\mathbf{B}(\cdot)$ represent non-linear vector and matrix functions respectively such that $\boldsymbol{a} : \mathbb{R}^{n_x} \to \mathbb{R}^{n_x}$ and $\mathbf{B} : \mathbb{R}^{n_x} \to \mathbb{R}^{n_x \times n_u}$. Presence of non-linearities in such set of ODEs establishes the fact that in general no analytical solution can be given and we usually rely on numerical techniques. These numerical techniques, described in detail in Brenan et al. (1989), include use of Euler explicit/implicit, Runge-Kutta, Backward differentiation formula, and Adams-Moulton method.

2.4 Summary of Problem Definition

We have introduced various forms of three basic parts of DO problem (objective functional (2.1), constraints (2.4), and process model in Section 2.3). These can be summarized to general OCP of following form

$$
\begin{aligned}
&\min_{\boldsymbol{u}(t),\boldsymbol{p}} \left\{ \mathcal{G}(\boldsymbol{x}(t_\mathrm{f}),\boldsymbol{p}) + \int_{t_0}^{t_\mathrm{f}} \mathcal{F}(\boldsymbol{x},\boldsymbol{u},\boldsymbol{p},t)\,\mathrm{d}t \right\}, \\
&\text{s.t.} \quad \dot{\boldsymbol{x}} = \boldsymbol{f}(\boldsymbol{x},\boldsymbol{u},\boldsymbol{p}), \quad \forall t \in [t_0,t_\mathrm{f}], \\
&\qquad \boldsymbol{x}(t_0,\boldsymbol{p}) = \boldsymbol{x}_0(\boldsymbol{p}), \\
&\qquad \boldsymbol{h}(\boldsymbol{x},\boldsymbol{u},\boldsymbol{p},t) = \boldsymbol{0}, \quad \forall t \in [t_0,t_\mathrm{f}], \\
&\qquad \boldsymbol{g}(\boldsymbol{x},\boldsymbol{u},\boldsymbol{p},t) \leq \boldsymbol{0}, \quad \forall t \in [t_0,t_\mathrm{f}], \\
&\qquad \boldsymbol{u}(t) \in [\boldsymbol{u}_\mathrm{min}(t),\boldsymbol{u}_\mathrm{max}(t)], \\
&\qquad \boldsymbol{p} \in [\boldsymbol{p}_\mathrm{min},\boldsymbol{p}_\mathrm{max}].
\end{aligned}
\tag{2.15}
$$

In order to find solution to this problem, one can exploit various techniques, stochastic (such as genetic algorithms, simulated annealing, etc.) or deterministic ones. Deterministic methods, in scope of this work, are based on following three principles: variational calculus (developed by Euler and Lagrange), dynamic programming (Bellman, 1957) and Pontryagin's minimum principle (Pontryagin et al., 1962). The latest one gave rise to most popular numerical techniques such as control vector parameterization, control vector iteration, boundary condition iteration, orthogonal collocation, and multiple shooting techniques.

Chapter 3

Solution of Optimal Control Problems

In this part we derive necessary conditions for optimality (NCO), which can identify candidates for solution of OCP. We introduce analytical methods of solving the OCPs. Next, we discuss how gradients to optimization criterion w.r.t. optimization variables can be gathered. These represent a key issue in solving the OCP numerically. Finally, we present a few most popular numerical methods used to solve the problem of optimal control.

3.1 Necessary Conditions for Optimality

Assume a minimization of functional of the form (2.7). For simplicity we will consider unconstrained case, however, we have already shown (in Section 2.2) that any constraint can be converted into canonical form of functional and thus NCO derived here easily extend to constrained cases. We point out any differences between constrained and unconstrained version of following derivation at appropriate places.

Minimized functional can be joined together with process equations (2.11) introducing vector of adjoint variables $\boldsymbol{\lambda}(t) \in \mathbb{R}^{n_x}$ (Note the same size of adjoint variables vector and states vector. That is why adjoint variables are sometimes called co-state variables.) such as

$$\mathcal{J} = \mathcal{G} + \int_{t_0}^{t_\mathrm{f}} [\mathcal{F} + \boldsymbol{\lambda}^T(\boldsymbol{f} - \dot{\boldsymbol{x}})] \,\mathrm{d}t. \tag{3.1}$$

We define Hamiltonian function as

$$H(\boldsymbol{x}, \boldsymbol{\lambda}, \boldsymbol{u}, \boldsymbol{p}, t) \equiv \mathcal{F}(\boldsymbol{x}, \boldsymbol{u}, \boldsymbol{p}, t) + \boldsymbol{\lambda}^T \boldsymbol{f}(\boldsymbol{x}, \boldsymbol{u}, \boldsymbol{p}). \tag{3.2}$$

In constrained case, Hamiltonian is defined in similar way and vector of adjoint variables is introduced likewise. Augmented forms of the Hamiltonian and the vector of adjoint variables can be defined similarly to augmented functional (2.8).

Now the minimized functional (3.1) takes form

$$\mathcal{J}(\boldsymbol{u},\boldsymbol{p}) = \mathcal{G}(\boldsymbol{x}(t_\mathrm{f}),\boldsymbol{x}(t_i),\boldsymbol{p},t_\mathrm{f},t_i) + \int_{t_0}^{t_\mathrm{f}} [H(\boldsymbol{x},\boldsymbol{\lambda},\boldsymbol{u},\boldsymbol{p},t) - \boldsymbol{\lambda}^T\dot{\boldsymbol{x}}]\,\mathrm{d}t, \tag{3.3}$$

where $i \in \{1,\ldots,n_i\}$ represents interior points considered. These represents either points where possible discontinuity in control profiles may arise or they can be considered as points where point constraints are evaluated.

For derivation of NCO of this functional we will assume type of problem of optimal process control where

- initial time is fixed (usually $t_0 = 0$),
- initial conditions are free ($\boldsymbol{x}(t_0,\boldsymbol{p}) = \boldsymbol{x}_0(\boldsymbol{p})$),
- as well as final conditions ($\boldsymbol{x}(t_\mathrm{f}) = \boldsymbol{x}_\mathrm{f}$),
- and final time (t_f).

Differential of functional (3.3) can be expressed as[1]

$$\mathrm{d}\mathcal{J} = \mathrm{d}\mathcal{G} + \int_{t_0}^{t_\mathrm{f}} \delta H\,\mathrm{d}t - \int_{t_0}^{t_\mathrm{f}} \delta(\boldsymbol{\lambda}^T\dot{\boldsymbol{x}})\,\mathrm{d}t + (H - \boldsymbol{\lambda}^T\dot{\boldsymbol{x}})|_{t_\mathrm{f}}\,\mathrm{d}t_\mathrm{f} + \sum_{i=1}^{n_i}[H - \boldsymbol{\lambda}^T\dot{\boldsymbol{x}}]_{t_i^+}^{t_i^-}\,\mathrm{d}t_i. \tag{3.4}$$

Consider now the term $\int_{t_0}^{t_\mathrm{f}} \delta(\boldsymbol{\lambda}^T\dot{\boldsymbol{x}})\,\mathrm{d}t$ which can be transformed using integration by parts into

$$\begin{aligned} -\int_{t_0}^{t_\mathrm{f}} \delta(\boldsymbol{\lambda}^T\dot{\boldsymbol{x}})\,\mathrm{d}t &= -\int_{t_0}^{t_\mathrm{f}} (\delta\boldsymbol{\lambda}^T\dot{\boldsymbol{x}} + \boldsymbol{\lambda}^T\delta\dot{\boldsymbol{x}})\,\mathrm{d}t, \\ &= \int_{t_0}^{t_\mathrm{f}} (\dot{\boldsymbol{\lambda}}^T\delta\boldsymbol{x} - \delta\boldsymbol{\lambda}^T\dot{\boldsymbol{x}})\,\mathrm{d}t - [\boldsymbol{\lambda}^T\delta\boldsymbol{x}]_{t_0}^{t_\mathrm{f}} - \sum_{i=1}^{n_i}[\boldsymbol{\lambda}^T\delta\boldsymbol{x}]_{t_i^+}^{t_i^-}. \end{aligned} \tag{3.5}$$

Expressing all differentials and variations in (3.4) and considering (3.5) we obtain (Please note that for purpose of better readability we use following notation $a_{t_i} \equiv a(t_i)$, where a

[1] For further explanation see Hull (2003).

stands for arbitrary variable and t_i may represent arbitrary time point.)

$$\begin{aligned}\mathrm{d}\mathcal{J} =&\frac{\partial \mathcal{G}}{\partial \boldsymbol{x}^T}\bigg|_{t=t_\mathrm{f}} \mathrm{d}\boldsymbol{x}_{t_\mathrm{f}} + \sum_{i=1}^{n_i} \frac{\partial \mathcal{G}}{\partial \boldsymbol{x}^T}\bigg|_{t=t_i} \mathrm{d}\boldsymbol{x}_{t_i} + \frac{\partial \mathcal{G}}{\partial \boldsymbol{p}^T}\mathrm{d}\boldsymbol{p} + \frac{\partial \mathcal{G}}{\partial t_\mathrm{f}}\mathrm{d}t_\mathrm{f} + \sum_{i=1}^{n_i} \frac{\partial \mathcal{G}}{\partial t_i}\mathrm{d}t_i \\ &+ \int_{t_0}^{t_\mathrm{f}} \left(\frac{\partial H}{\partial \boldsymbol{x}^T}\delta\boldsymbol{x} + \frac{\partial H}{\partial \boldsymbol{\lambda}^T}\delta\boldsymbol{\lambda} + \frac{\partial H}{\partial \boldsymbol{u}^T}\delta\boldsymbol{u} + \frac{\partial H}{\partial \boldsymbol{p}^T}\delta\boldsymbol{p} + \dot{\boldsymbol{\lambda}}^T\delta\boldsymbol{x} - \delta\boldsymbol{\lambda}^T\dot{\boldsymbol{x}} \right)\mathrm{d}t \\ &- \boldsymbol{\lambda}_{t_\mathrm{f}}^T\delta\boldsymbol{x}_{t_\mathrm{f}} + \boldsymbol{\lambda}_{t0}^T\delta\boldsymbol{x}_{t0} + \sum_{i=1}^{n_i}(\boldsymbol{\lambda}_{t_i^+}^T\delta\boldsymbol{x}_{t_i^+} - \boldsymbol{\lambda}_{t_i^-}^T\delta\boldsymbol{x}_{t_i^-}) + H_{t_\mathrm{f}}\mathrm{d}t_\mathrm{f} - \boldsymbol{\lambda}_{t_\mathrm{f}}^T\dot{\boldsymbol{x}}_{t_\mathrm{f}}\mathrm{d}t_\mathrm{f} \\ &+ \sum_{i=1}^{n_i}(H_{t_i^-} - H_{t_i^+})\,\mathrm{d}t_i + \sum_{i=1}^{n_i}(\boldsymbol{\lambda}_{t_i^+}^T\dot{\boldsymbol{x}}_{t_i^+} - \boldsymbol{\lambda}_{t_i^-}^T\dot{\boldsymbol{x}}_{t_i^-})\,\mathrm{d}t_i.\end{aligned} \tag{3.6}$$

Regrouping the corresponding terms together, noting that $\mathrm{d}\boldsymbol{x}_{t_i} = \delta\boldsymbol{x}_{t_i^\pm} + \dot{\boldsymbol{x}}_{t_i^\pm}\mathrm{d}t_i$ and equating $\delta\boldsymbol{x}_{t_0} = \left(\frac{\partial \boldsymbol{x}_0^T}{\partial \boldsymbol{p}}\right)^T \mathrm{d}\boldsymbol{p}$ we get

$$\begin{aligned}\mathrm{d}\mathcal{J} =& \left(\frac{\partial \mathcal{G}}{\partial \boldsymbol{x}^T}\bigg|_{t_\mathrm{f}} - \boldsymbol{\lambda}_{t_\mathrm{f}}^T \right)\mathrm{d}\boldsymbol{x}_{t_\mathrm{f}} + \left(\frac{\partial \mathcal{G}}{\partial t_\mathrm{f}} + H_{t_\mathrm{f}} \right)\mathrm{d}t_\mathrm{f} + \left(\frac{\partial \mathcal{G}}{\partial \boldsymbol{p}} + \int_{t_0}^{t_\mathrm{f}} \frac{\partial H}{\partial \boldsymbol{p}}\,\mathrm{d}t + \frac{\partial \boldsymbol{x}_0^T}{\partial \boldsymbol{p}}\boldsymbol{\lambda}_{t0} \right)\mathrm{d}\boldsymbol{p}^T \\ &+ \sum_{i=1}^{n_i}\left(\frac{\partial \mathcal{G}}{\partial \boldsymbol{x}^T}\bigg|_{t=t_i} + \boldsymbol{\lambda}_{t_i^+}^T - \boldsymbol{\lambda}_{t_i^-}^T \right)\mathrm{d}\boldsymbol{x}_{t_i} + \sum_{i=1}^{n_i}\left(\frac{\partial \mathcal{G}}{\partial t_i} + H_{t_i^-} - H_{t_i^+} \right)\mathrm{d}t_i \\ &+ \int_{t_0}^{t_\mathrm{f}} \left[\left(\frac{\partial H}{\partial \boldsymbol{x}^T} + \dot{\boldsymbol{\lambda}}^T \right)\delta\boldsymbol{x} + \left(\frac{\partial H}{\partial \boldsymbol{\lambda}^T} - \dot{\boldsymbol{x}}^T \right)\delta\boldsymbol{\lambda} + \frac{\partial H}{\partial \boldsymbol{u}^T}\,\delta\boldsymbol{u} \right]\mathrm{d}t.\end{aligned} \tag{3.7}$$

The conditions for optimality follow directly from the equation (3.7). Differential of functional $\mathcal{J}$ must be zero at optimum. That is why all bracketed terms in equation (3.7) must be zero which gives necessary conditions for optimality in following form

- optimality (extremal) condition for control variables

$$\frac{\partial H}{\partial \boldsymbol{u}} = \boldsymbol{0}, \quad \forall t \in [t_0, t_\mathrm{f}], \tag{3.8a}$$

- optimality condition for parameters

$$\frac{\partial \mathcal{G}}{\partial \boldsymbol{p}} - \int_{t_0}^{t_\mathrm{f}} \frac{\partial H}{\partial \boldsymbol{p}}\,\mathrm{d}t + \frac{\partial \boldsymbol{x}_0^T}{\partial \boldsymbol{p}}\boldsymbol{\lambda}(t_0) = \boldsymbol{0}, \tag{3.8b}$$

- adjoint variables definition

$$\dot{\boldsymbol{\lambda}} = -\frac{\partial H}{\partial \boldsymbol{x}}, \qquad \forall t \in [t_0, t_\mathrm{f}], \tag{3.8c}$$

- adjoint variables boundary conditions

$$\boldsymbol{\lambda}_{t_\mathrm{f}} = \left.\frac{\partial \mathcal{G}}{\partial \boldsymbol{x}}\right|_{t=t_\mathrm{f}}, \tag{3.8d}$$

- optimality condition for final time

$$\frac{\partial \mathcal{G}}{\partial t_\mathrm{f}} + H(t_\mathrm{f}) = 0, \tag{3.8e}$$

- optimality conditions for switching times

$$\frac{\partial \mathcal{G}}{\partial t_i} + H(t_i^-) - H(t_i^+) = 0, \qquad \forall i \in \overline{1, n_i}, \tag{3.8f}$$

- adjoint variables switching conditions

$$\left.\frac{\partial \mathcal{G}}{\partial \boldsymbol{x}}\right|_{t=t_i} + \boldsymbol{\lambda}(t_i^+) - \boldsymbol{\lambda}(t_i^-) = \mathbf{0}, \qquad \forall i \in \overline{1, n_i}, \tag{3.8g}$$

- condition for optimal state variables

$$\dot{\boldsymbol{x}} = \frac{\partial H}{\partial \boldsymbol{\lambda}}, \qquad \forall t \in [t_0, t_\mathrm{f}], \tag{3.8h}$$

- condition for Lagrange multipliers (Karush-Kuhn-Tucker conditions):

$$\nu_c \mathcal{J}_c = 0,\ \nu_c \geq 0, \qquad \forall c \in \mathbb{I}, \tag{3.8i}$$

  where $\mathbb{I}$ represents set of point inequality constraints. These conditions give so-called *complementary slackness* condition and they apply only in the case of minimization of constrained functionals.

Moreover, if treated OCP is in autonomous form, i.e. functions $\boldsymbol{f}(\cdot)$ and $\mathcal{F}(\cdot)$ are not explicit functions of time, we can use conditions (3.8c) and (3.8h) to state that

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{\partial H}{\partial \boldsymbol{x}^T}\dot{\boldsymbol{x}} + \frac{\partial H}{\partial \boldsymbol{\lambda}^T}\dot{\boldsymbol{\lambda}} + \frac{\partial H}{\partial \boldsymbol{u}^T}\dot{\boldsymbol{u}} + \frac{\partial H}{\partial \boldsymbol{p}^T}\dot{\boldsymbol{p}} = 0, \qquad \forall t \in [t_0, t_\mathrm{f}], \tag{3.9}$$

and so optimal Hamiltonian is constant over the time.

It should be noted that (Bryson, Jr. and Ho, 1975) necessary condition for minimum of functional may be established with second-order conditions as

$$\frac{\partial^2 H}{\partial \boldsymbol{u} \partial \boldsymbol{u}^T} \geq 0, \qquad \forall t \in [t_0, t_\mathrm{f}], \tag{3.10}$$

where the used inequality denotes positive semi-definiteness of the matrix.

3.2 Analytical Methods

Historically, the development of analytical methods for solving OCPs had always reflected the current needs of optimization theory and engineering. Variational calculus, created by Euler and Lagrange, represented the first standalone framework to find trajectories with specified minimum/maximum properties. They aimed to provide mathematical apparatus for treating mainly theoretical problems such as brachistochrone problem, finding the shape of a wire along which the point-like body move from one given point to another under the action of gravity force in minimum time.

Their work was further extended by the works of Legendre, Hamilton, and Weierstrass. The last century saw an enormous rise of interest in flight and rocket industry as well as in space research. All these fields required to solve various optimal control problems. However, variational calculus appeared to be either impractical to use or its important features were overlooked. These circumstances gave rise to theory of *dynamic programming* by american school of Richard Bellman (in 1950s) and *maximum/minimum principle* by russian group of Lev Semyonovich Pontryagin (in 1960s).

3.2.1 Calculus of Variations

As mentioned above, calculus of variations represents a theoretical tool for optimizing trajectories and so the fundamental problem of calculus of variations may be written in following form

$$\min_{\boldsymbol{x}(t)} \int_{t_0}^{t_\mathrm{f}} \mathcal{F}(\dot{\boldsymbol{x}}, \boldsymbol{x}, t)\, \mathrm{d}\boldsymbol{x}. \tag{3.11}$$

This functional does not involve control $\boldsymbol{u}$, however, this can be easily incorporated as shown in Pontryagin et al. (1962). The same applies for vector of parameters $\boldsymbol{p}$. The main result of calculus of variations is Euler-Lagrange equation

$$\frac{\partial \mathcal{F}}{\partial \boldsymbol{x}} - \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial \mathcal{F}}{\partial \dot{\boldsymbol{x}}} = 0, \tag{3.12}$$

which gives necessary condition of optimality which can be shown to be equivalent to the condition (3.8c). The drawback of the method of calculus of variations lies in inability to tackle the problem of constrained control which appears naturally in most of the problems arising in practical (engineering) applications.

3.2.2 Dynamic Programming

This method is based on the Bellman's principle of optimality (Bellman, 1957) which says that "Optimal trajectory is piece-wise optimal.". Dynamic Programming defines a concept of optimal cost-to-go or value function as

$$\mathcal{J}^\star(\boldsymbol{x},t) = \min_{\substack{\boldsymbol{u}\in[\boldsymbol{u}_{\min},\boldsymbol{u}_{\max}]\\ \boldsymbol{p}\in[\boldsymbol{p}_{\min},\boldsymbol{p}_{\max}]}} \left\{ \int_t^{t_\mathrm{f}} \mathcal{F}(\boldsymbol{x},\boldsymbol{u},\boldsymbol{p},\tau)\,\mathrm{d}\tau + \mathcal{G}(\boldsymbol{x}(t_\mathrm{f}),\boldsymbol{p},t_\mathrm{f}) \right\}. \tag{3.13}$$

According to this function, the optimal control $\boldsymbol{u}$ is found as a solution Hamilton-Jacobi-Bellman partial differential equation

$$-\frac{\partial \mathcal{J}^\star(\boldsymbol{x},t)}{\partial t} = \min_{\substack{\boldsymbol{u}\in[\boldsymbol{u}_{\min},\boldsymbol{u}_{\max}]\\ \boldsymbol{p}\in[\boldsymbol{p}_{\min},\boldsymbol{p}_{\max}]}} \left\{ \mathcal{F}(\boldsymbol{x},\boldsymbol{u},\boldsymbol{p},t) + \frac{\partial \mathcal{J}^\star(\boldsymbol{x},t)}{\partial \boldsymbol{x}^T}\boldsymbol{f}(\boldsymbol{x},\boldsymbol{u},\boldsymbol{p}) \right\}. \tag{3.14}$$

This equation provides sufficient condition of optimality when solved over the whole state space. However, with higher state dimensions this may become impractical. This feature is referred, by own words of Richard Bellman, as a *curse of dimensionality*.

3.2.3 Pontryagin's Minimum Principle

This principle, formulated in Pontryagin et al. (1962), can be regarded as an extension to method of calculus of variations for problems with constrained controls. In certain sense, it stands as an alternative to Dynamic Programming which can be shown to be equivalent to this principle. It can be proven that optimal control is the one which solves this problem

$$\min_{\substack{\boldsymbol{u}\in[\boldsymbol{u}_{\min},\boldsymbol{u}_{\max}]\\ \boldsymbol{p}\in[\boldsymbol{p}_{\min},\boldsymbol{p}_{\max}]}} \quad H(\boldsymbol{x},\boldsymbol{\lambda},\boldsymbol{u},\boldsymbol{p},t) \tag{3.15}$$

$$\text{s.t.} \quad \dot{\boldsymbol{x}} = \boldsymbol{f}(\boldsymbol{x},\boldsymbol{u},\boldsymbol{p}), \qquad \boldsymbol{x}(t_0,\boldsymbol{p}) = \boldsymbol{x}_0(\boldsymbol{p}), \tag{3.16}$$

$$\dot{\boldsymbol{\lambda}} = -\frac{\partial H}{\partial \boldsymbol{x}}, \qquad \boldsymbol{\lambda}(t_\mathrm{f}) = \left.\frac{\partial \mathcal{G}}{\partial \boldsymbol{x}}\right|_{t_\mathrm{f}}. \tag{3.17}$$

Pontryagin's Minimum Principle (PMP) stands for necessary condition of optimality and therefore the pair of controls $\boldsymbol{u}^*$ and parameters $\boldsymbol{p}^*$ which solve the problem is a candidate for solution of OCP (2.15). Our further discussions on OCPs consider use of this principle in preference.

Example 1: PMP for quadratic Lagrange functional and linear time invariant process model.

The problem is to minimize functional (2.2c) subject to process model (2.12). The Hamiltonian, in this case, reads as

$$H \equiv \frac{1}{2}\boldsymbol{x}^T\mathbf{Q}\boldsymbol{x} + \frac{1}{2}\boldsymbol{u}^T\mathbf{R}\boldsymbol{u} + \boldsymbol{\lambda}^T(\mathbf{A}\boldsymbol{x} + \mathbf{B}\boldsymbol{u}). \tag{3.18}$$

Hamiltonian is convex quadratic function and thus its minimum is bounded from below and it is achieved via satisfaction of NCO which give

$$-\frac{\partial H}{\partial \boldsymbol{x}} = \dot{\boldsymbol{\lambda}} = -\mathbf{Q}\boldsymbol{x} - \mathbf{A}^T\boldsymbol{\lambda}, \qquad \boldsymbol{\lambda}(t_\mathrm{f}) = \mathbf{0}, \tag{3.19}$$

$$\frac{\partial H}{\partial \boldsymbol{u}} = \mathbf{0} = \mathbf{R}\boldsymbol{u} + \mathbf{B}^T\boldsymbol{\lambda}. \tag{3.20}$$

These conditions give expressions for optimal control variables (if these are unconstrained)

$$\boldsymbol{u}^* = -\mathbf{R}^{-1}\mathbf{B}^T\boldsymbol{\lambda}, \tag{3.21}$$

and for state and adjoint variables such that

$$\dot{\boldsymbol{x}}^* = \mathbf{A}\boldsymbol{x}^* - \mathbf{B}\mathbf{R}^{-1}\mathbf{B}^T\boldsymbol{\lambda}^*, \qquad \boldsymbol{x}^*(t_0) = \boldsymbol{x}_0, \tag{3.22a}$$

$$\dot{\boldsymbol{\lambda}}^* = -\mathbf{Q}\boldsymbol{x}^* - \mathbf{A}^T\boldsymbol{\lambda}^*, \qquad \boldsymbol{\lambda}^*(t_\mathrm{f}) = \mathbf{0}. \tag{3.22b}$$

This system of linear ODEs with boundary conditions represents two-point boundary value problem (TPBVP) which requires to be resolved in order to find optimal trajectories of $\boldsymbol{x}^*$, $\boldsymbol{u}^*$, and $\boldsymbol{\lambda}^*$. In closed-loop optimal control, this leads to solving of Ricatti matrix differential equation to arrive at expression for optimal feedback control law in the form $\boldsymbol{u}^* = \mathbf{K}\boldsymbol{x}^*$, where $\mathbf{K} \in \mathbb{R}^{n_u \times n_x}$.

Example 2: PMP for control affine Lagrange functional and control affine process model.

The problem is to find such optimal control which will minimize the functional

$$\mathcal{F} \equiv F_0(\boldsymbol{x}) + \sum_{i=1}^{n_u} F_i(\boldsymbol{x})u_i \tag{3.23}$$

which may represent minimum control effort problem[2] (2.2a) or minimum time problem (2.2b) as well. This minimization is done subject to the input (control) affine process model (2.14) which final state $\boldsymbol{x}(t_\mathrm{f})$ may be fixed or free.

Use of PMP results in

$$\min_{\boldsymbol{u}\in[\boldsymbol{u}_\mathrm{min},\boldsymbol{u}_\mathrm{max}]} H \equiv \min_{\boldsymbol{u}\in[\boldsymbol{u}_\mathrm{min},\boldsymbol{u}_\mathrm{max}]} \left\{ H_0(\boldsymbol{x},\boldsymbol{\lambda}) + \sum_{i=1}^{n_u} H_i(\boldsymbol{x},\boldsymbol{\lambda}) u_i \right\} \tag{3.24}$$

$$\text{s.t.} \quad \dot{\boldsymbol{x}} = \boldsymbol{a}(\boldsymbol{x}) + \mathbf{B}(\boldsymbol{x})\boldsymbol{u}, \qquad \boldsymbol{x}(t_0) = \boldsymbol{x}_0, \tag{3.25}$$

$$\dot{\boldsymbol{\lambda}} = -\frac{\partial H}{\partial \boldsymbol{x}}, \qquad \boldsymbol{\lambda}(t_\mathrm{f}) = \begin{cases} \frac{\partial \mathcal{G}}{\partial x_i}\big|_{t_\mathrm{f}}, & \text{if } x_i(t_\mathrm{f}) \text{ is free,} \\ \nu_i, & \text{if } x_i(t_\mathrm{f}) \text{ is fixed.} \end{cases} \tag{3.26}$$

where

$$H_0(\boldsymbol{x},\boldsymbol{\lambda}) = F_0(\boldsymbol{x}) + \boldsymbol{\lambda}^T \boldsymbol{a}(\boldsymbol{x}), \tag{3.27}$$

$$H_i(\boldsymbol{x},\boldsymbol{\lambda}) = F_i(\boldsymbol{x}) + \boldsymbol{\lambda}^T \boldsymbol{b}_i(\boldsymbol{x}), \tag{3.28}$$

and $\boldsymbol{b}_i(\boldsymbol{x})$ stands for the ith column of $\mathbf{B}(\boldsymbol{x})$. Hamiltonian is affine in control variables and thus its minimization is achieved by following conditions for optimal control

$$u_i^* = \begin{cases} u_{i,\mathrm{min}} & \text{if } H_i(\boldsymbol{x},\boldsymbol{\lambda}) > 0, \\ u_{i,\mathrm{max}} & \text{if } H_i(\boldsymbol{x},\boldsymbol{\lambda}) < 0, \\ ? & \text{if } H_i(\boldsymbol{x},\boldsymbol{\lambda}) = 0. \end{cases} \tag{3.29}$$

Hence, the optimal control is either hitting the constraints (bang-bang control) or it is undetermined (so-called singular control or control on singular arc, $\boldsymbol{u}_\mathrm{sing}$) when the switching function $H_i(\boldsymbol{x},\boldsymbol{\lambda}) = 0$.

In order to determine the singular control, we use switching function and its derivatives w.r.t. time such that

$$H_i(\boldsymbol{x},\boldsymbol{\lambda}) = \dot{H}_i(\boldsymbol{x},\boldsymbol{\lambda}) = \ddot{H}_i(\boldsymbol{x},\boldsymbol{\lambda}) = \cdots = 0. \tag{3.30}$$

It can be easily shown that such conditions yield system of homogeneous equations linear in $\boldsymbol{\lambda}$. Such system, $\mathbf{A}(\boldsymbol{x},\boldsymbol{u})\boldsymbol{\lambda} = \mathbf{0}$, possesses a non-trivial solution if and only if $\det(\mathbf{A}(\boldsymbol{x},\boldsymbol{u})) = 0$. Using this condition, singular control, $\boldsymbol{u}_\mathrm{sing}$, can be found as a function of state variables (state feedback control law).

[2] In this case, an ℓ_1 norm is used in the objective and controls are restricted to not change a sign.

3.3 Numerical Methods

Here, we present the most popular numerical methods which are based on PMP and NCO. As mentioned above, there are various numerical methods which are capable of solving OCPs. Even though these methods provide approximate solution, in practice they can converge very closely to the exact solution based on the selected accuracy.

They are based either on indirect (optimize-then-discretize) or direct (discretize-then-optimize) approaches. Indirect approaches evaluate optimality conditions at first and then try to resolve resulting TPBVP, which arise typically (as we have seen in examples on the use of PMP). This resolution is then done by iterative calculus which uses techniques like discretization and/or gradient-based resolution.

Direct approaches use discretization of control variables (sequential approach) or control and state variables (simultaneous approach) first in order to translate the problem of dynamic optimization into the static one. Approximate solution to OCP is then obtained as a solution of the problem of non-linear programming (NLP) which uses gradient-based techniques to arrive at optimum. There exists a large number of papers which classifies the numerical methods and discusses their advantages and drawbacks (Bryson, Jr. and Ho, 1975; Goh and Teo, 1988; Srinivasan et al., 2003). Such methods include:

- Indirect Methods

  Control Vector Iteration (CVI)

  Boundary Condition Iteration (BCI)

- Direct Methods

  Complete Discretization

  Control Vector Parameterization (CVP)

  Direct Multiple Shooting

3.3.1 Control Vector Iteration

The CVI method is based on resolution of TPBVP by adapting the control trajectories using direct sensitivity of the Hamiltonian to the control. New guess for control trajectories $\boldsymbol{u}^{k+1}$ is computed using the old one, $\boldsymbol{u}^k$, by following adaptation formula

$$\boldsymbol{u}^{k+1} = \boldsymbol{u}^k - \gamma \frac{\partial H}{\partial \boldsymbol{u}}, \tag{3.31}$$

where $\gamma \in (0, 1]$ is a numerical parameter, in fact the length of the step. The whole procedure is initialized by the guess $\boldsymbol{u}^0$. The main part of this procedure then resolves process model equations (using ODE solver) by forward integration. Next, ODEs for adjoint variables are integrated backwards. Finally, new guess for control trajectories is taken and whole procedure is repeated until the optimality condition (3.8a) is satisfied.

3.3.2 Boundary Condition Iteration

This method solves the TPBVP by successive update of the guesses for boundary conditions $\boldsymbol{\lambda}(t_0)$. Initially, the guess $\boldsymbol{\lambda}^0(t_0)$ is used to integrate the systems of ODEs for state and adjoint variables forward in time. Values of $\boldsymbol{\lambda}^0(t_\mathrm{f})$ obtained by integration is then compared with optimality condition (3.8d). If these are not in accord, a new guess of initial conditions for adjoint variables is made and the whole procedure is repeated until they are equal within specified tolerance. This update may be done e.g. using evaluated sensitivity of the $\boldsymbol{\lambda}(t)$ trajectory to this initial condition.

3.3.3 Complete Discretization

Complete discretization, known as well as simultaneous approach, is based on discretization of both state and control trajectories (Biegler, 1984; Tsang et al., 1975; Čižniar et al., 2005). This can be efficiently done by using orthogonal collocation (OC) on finite elements to establish a piece-wise polynomial approximation of these trajectories on some chosen number (n_e) of intervals (elements). Approximation of the state and control trajectories on the kth interval is then as follows

$$\hat{\boldsymbol{x}}^k(t) = \sum_{i=0}^{n_{cp}} \hat{\boldsymbol{x}}_i^k \, \phi_i(t), \qquad \text{with } \phi_i(t) = \prod_{j=0, j\neq i}^{n_{cp}} \frac{t - t_j^k}{t_i^k - t_j^k}, \tag{3.32a}$$

$$\hat{\boldsymbol{u}}^k(t) = \sum_{i=1}^{n_{cp}} \hat{\boldsymbol{u}}_i^k \, \psi_i(t), \qquad \text{with } \psi_i(t) = \prod_{j=1, j\neq i}^{n_{cp}} \frac{t - t_j^k}{t_i^k - t_j^k}, \tag{3.32b}$$

where $\hat{\boldsymbol{x}}_i^k$ ($\hat{\boldsymbol{u}}_i^k$) represents vector of approximated values of state (control) variables at the ith collocation point, i.e. at time t_i^k and functions $\phi_i(t)$ and $\psi_i(t)$ represent Lagrange polynomials which is the set of basis polynomial functions usually used by this method. This is illustrated in Figure 3.1 which shows three consecutive intervals of approximation of trajectory of an arbitrary state variable. Points t_i^k are usually chosen as roots of n_{cp}–th

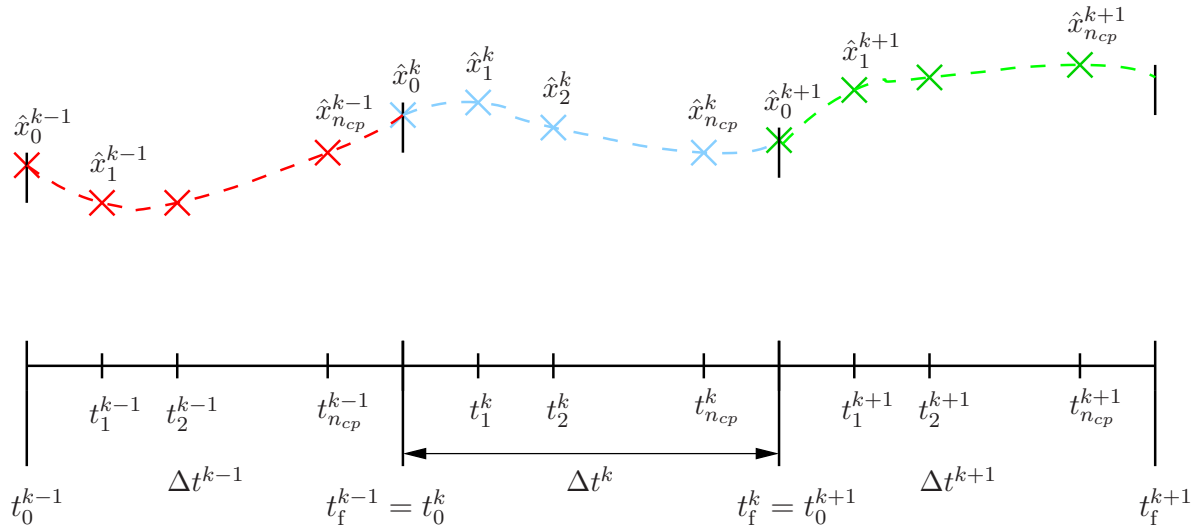


Figure 3.1: Schematic representation of the orthogonal collocation on finite elements.

degree Legendre polynomial. Using this piece-wise polynomial approximation, we can reformulate OCP (2.15) into the algebraic form

$$
\begin{aligned}
\min_{\substack{\hat{\boldsymbol{x}}_i^k, \hat{\boldsymbol{u}}_i^k, \boldsymbol{p} \\ \forall i \in \overline{1,n_{cp}},\ \forall k \in \overline{1,n_e}}} \quad & \left\{ \mathcal{G}(\hat{\boldsymbol{x}}^{n_e}(t_{\mathrm{f}}^{n_e}), \boldsymbol{p}) + \sum_{k=1}^{n_e} \int_{t_0^k}^{t_{\mathrm{f}}^k} \mathcal{F}(\hat{\boldsymbol{x}}^k, \hat{\boldsymbol{u}}^k, \boldsymbol{p}, t)\, \mathrm{d}t \right\}, \\
\text{s.t.} \quad & \dot{\hat{\boldsymbol{x}}}^k = \boldsymbol{f}(\hat{\boldsymbol{x}}^k, \hat{\boldsymbol{u}}^k, \boldsymbol{p}), \quad \forall i \in \overline{1, n_{cp}},\ \forall k \in \overline{1, n_e}, \\
& \hat{\boldsymbol{x}}^1(t_0^1, \boldsymbol{p}) = \boldsymbol{x}_0(\boldsymbol{p}), \\
& \hat{\boldsymbol{x}}^k(t_0^k) = \hat{\boldsymbol{x}}^{k-1}(t_{\mathrm{f}}^{k-1}), \quad \forall k \in \overline{2, n_e}, \\
& \boldsymbol{h}(\hat{\boldsymbol{x}}^k, \hat{\boldsymbol{u}}^k, \boldsymbol{p}, t) = \boldsymbol{0}, \quad \forall t \in [t_0^k, t_{\mathrm{f}}^k],\ \forall k \in \overline{1, n_e}, \\
& \boldsymbol{g}(\hat{\boldsymbol{x}}^k, \hat{\boldsymbol{u}}^k, \boldsymbol{p}, t) \leq \boldsymbol{0}, \quad \forall t \in [t_0^k, t_{\mathrm{f}}^k],\ \forall k \in \overline{1, n_e}, \\
& \hat{\boldsymbol{u}}_i^k \in [\hat{\boldsymbol{u}}_{i,\min}^k, \hat{\boldsymbol{u}}_{i,\max}^k], \quad \forall i \in \overline{1, n_{cp}},\ \forall k \in \overline{1, n_e}, \\
& \boldsymbol{p} \in [\boldsymbol{p}_{\min}, \boldsymbol{p}_{\max}].
\end{aligned}
\tag{3.33}
$$

The resulting NLP program can be handled using standard techniques, such as by sequential quadratic programming (SQP) or interior-point (IP) solvers. Size of the problem depends on chosen accuracy of the approximation (number of elements and collocation points). Although the resulting NLP may become quite big, if high accuracy of the polynomial approximation is desired, it would be sparse as well and such feature can be efficiently exploited by modern NLP solvers. This property together with no need to solve any IVPs (if their solution is costly or numerically unstable) makes complete discretization and OC

approaches of the most popular frameworks in numerical dynamic optimization. On the other hand, this approach is of so-called *infeasible* type, i.e. the process model equations are satisfied only if the optimal solution is found.

3.3.4 Control Vector Parameterization

This method, see Goh and Teo (1988); Hirmajer et al. (2008), is among the most popular numerical procedures for handling the OCP because of the straightforward nature of the idea behind and due to the relative easiness of implementation.

In the first step of this method, control trajectory $\boldsymbol{u}(t)$ is discretized (parameterized) on finite number (n_e) of intervals considering polynomial control on each of these intervals (segments). Resulting control approximation is of piece-wise polynomial nature. We may consider

- piece-wise constant (PWC) segments

$$\hat{\boldsymbol{u}}(t) = \sum_{k=1}^{n_e} \hat{\boldsymbol{u}}^k \chi^k(t), \qquad \chi^k(t) = \begin{cases} 1 & \text{if } t \in [t^{k-1}, t^k], \\ 0 & \text{otherwise,} \end{cases} \tag{3.34}$$

- piece-wise affine segments

$$\hat{\boldsymbol{u}}(t) = \hat{\boldsymbol{u}}^{k-1} + \frac{\hat{\boldsymbol{u}}^k - \hat{\boldsymbol{u}}^{k-1}}{t^k - t^{k-1}}(t - t^{k-1}), \qquad \forall k \in \overline{1, n_e}. \tag{3.35}$$

- general piece-wise polynomial segments – we may adopt the approximation by Lagrange polynomials (3.32b)

In this work, we are mostly dealing with PWC control. Using this approach we aim to numerically determine the optimal values of a vector of parameters

$$\boldsymbol{y} = (\hat{\boldsymbol{u}}^1, \hat{\boldsymbol{u}}^2, \ldots, \hat{\boldsymbol{u}}^{n_e}, \Delta t^1, \Delta t^2, \ldots, \Delta t^{n_e}, \boldsymbol{p})^T$$

with constant control over kth interval ($k = 1, \ldots, n_e$) with length $\Delta t^k = t_{\mathrm{f}}^k - t_0^k$. Using proposed discretization (parameterization) the problem (2.15) is transformed into NLP

problem of the form

$$\begin{aligned}
&\min_{\boldsymbol{y}} \left\{ \mathcal{G}(\boldsymbol{x}(t_{\mathrm{f}}^{n_e}), \boldsymbol{p}) + \sum_{k=1}^{n_e} \int_{t_0^k}^{t_{\mathrm{f}}^k} \mathcal{F}(\boldsymbol{x}, \hat{\boldsymbol{u}}^k, \boldsymbol{p}, t)\, \mathrm{d}t \right\}, \\
&\text{s.t. } \dot{\boldsymbol{x}} = \boldsymbol{f}(\boldsymbol{x}, \hat{\boldsymbol{u}}^k, \boldsymbol{p}), \quad \forall t \in [t_0^k, t_{\mathrm{f}}^k],\ \forall k \in \overline{1, n_e}, \\
&\quad \boldsymbol{x}(t_0^1, \boldsymbol{p}) = \boldsymbol{x}_0(\boldsymbol{p}), \\
&\quad \boldsymbol{h}(\boldsymbol{x}, \hat{\boldsymbol{u}}^k, \boldsymbol{p}, t) = 0, \quad \forall t \in [t_0, t_{\mathrm{f}}],\ \forall k \in \overline{1, n_e}, \\
&\quad \boldsymbol{g}(\boldsymbol{x}, \hat{\boldsymbol{u}}^k, \boldsymbol{p}, t) \leq 0, \quad \forall t \in [t_0^k, t_{\mathrm{f}}^k],\ \forall k \in \overline{1, n_e}, \\
&\quad \hat{\boldsymbol{u}}^k(t) \in [\hat{\boldsymbol{u}}_{\min}^k(t), \hat{\boldsymbol{u}}_{\max}^k(t)], \quad \forall k \in \overline{1, n_e}, \\
&\quad \boldsymbol{p} \in [\boldsymbol{p}_{\min}, \boldsymbol{p}_{\max}].
\end{aligned} \tag{3.36}$$

This is a static NLP problem with embedded set of differential equations. It can be resolved by any gradient–based method (SQP or IP method) while using some efficient numerical differential equation solver.

The evaluation of objective function is carried out by solving an IVP problem and gradients of the objective function and constraints w.r.t.decision variables can be evaluated by using of the finite differences (FD), sensitivity equations (SE) (Feehery, 1998), or adjoint variables (AV) (Hirmajer and Fikar, 2007) method. These methods are associated with additional solving of IVPs and will be explained later in this text.

CVP method algorithm. Optimization procedure is depicted in Figure (3.2) and can be described in following steps:

Step 1. Make initial guess for values of $\boldsymbol{y}$.

Step 2. Solve the process model, use ODE solver to integrate IVP (2.10).

Step 3. Evaluate objective functional and constraint functions.

Step 4. Use FD, SE, or AV method to gather the gradients.

Step 5. If the optimality conditions are satisfied then quit.
Else, use NLP solver to get new guess for $\boldsymbol{y}$ and go to Step 2.

3.3.5 Direct Multiple Shooting

This method stands in the middle of latter two methods. Direct Multiple Shooting, introduced by Bock and Plitt (1984), considers piece-wise polynomial parameterization of control trajectories. State variables trajectories are, however, considered to be sequentially numerically integrated on some chosen number of time intervals, n_e.

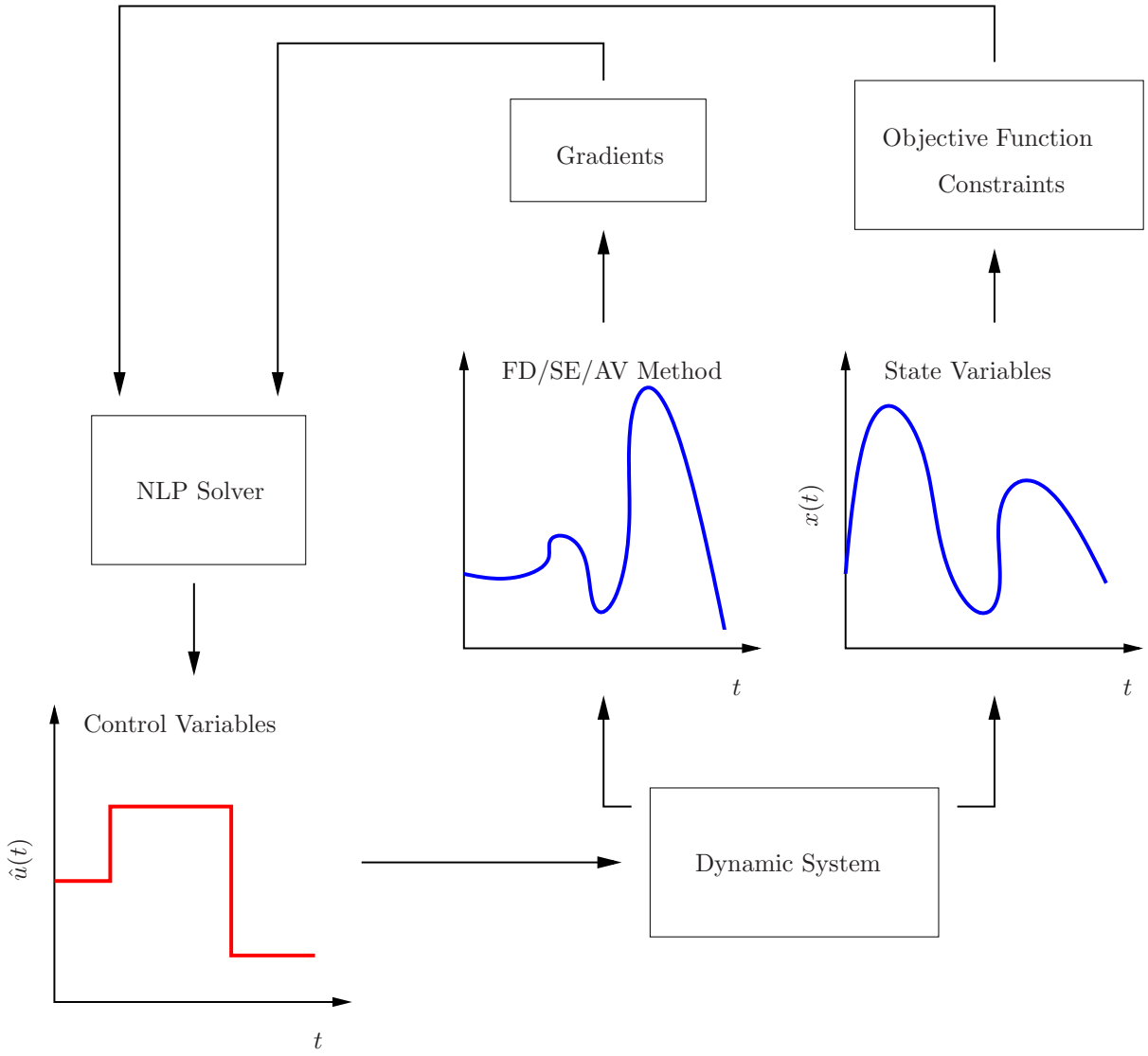


Figure 3.2: Control vector parameterization algorithm.

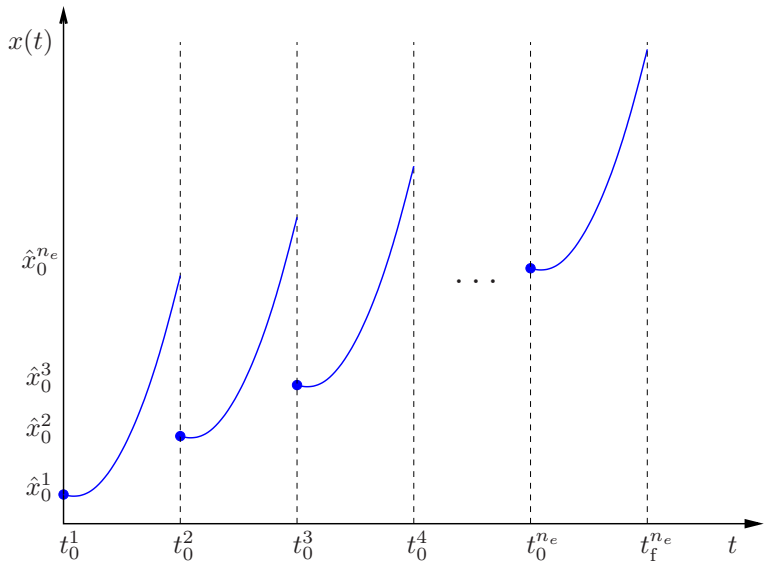


Figure 3.3: Principle of direct multiple shooting.

This is illustrated in Fig. 3.3. The vector of initial conditions $(\hat{\boldsymbol{x}}_0^1, \hat{\boldsymbol{x}}_0^2, \ldots, \hat{\boldsymbol{x}}_0^{n_e})^T$ is considered to be joined among the vector of decision variables, $\boldsymbol{y}$. Additional set of affine constraints is then considered to enforce the continuity state trajectories. The resulting NLP problem reads as follows

$$
\begin{aligned}
\min_{\boldsymbol{y}} \; & \left\{ \mathcal{G}(\boldsymbol{x}(t_\mathrm{f}^{n_e}), \boldsymbol{p}) + \sum_{k=1}^{n_e} \int_{t_0^k}^{t_\mathrm{f}^k} \mathcal{F}(\boldsymbol{x}, \hat{\boldsymbol{u}}^k, \boldsymbol{p}, t)\, \mathrm{d}t \right\}, \\
\text{s.t. } & \dot{\boldsymbol{x}} = \boldsymbol{f}(\boldsymbol{x}, \hat{\boldsymbol{u}}^k, \boldsymbol{p}), \quad \forall t \in [t_0^k, t_\mathrm{f}^k],\ \forall k \in \overline{1, n_e}, \\
& \hat{\boldsymbol{x}}_0^1 = \boldsymbol{x}_0(\boldsymbol{p}), \\
& \boldsymbol{x}(t_0^k) = \hat{\boldsymbol{x}}_0^k, \quad \forall k \in \overline{1, n_e}, \\
& \boldsymbol{x}(t_\mathrm{f}^{k-1}) = \hat{\boldsymbol{x}}_0^k, \quad \forall k \in \overline{2, n_e}, \\
& \boldsymbol{h}(\boldsymbol{x}, \hat{\boldsymbol{u}}^k, \boldsymbol{p}, t) = 0, \quad \forall t \in [t_0, t_\mathrm{f}],\ \forall k \in \overline{1, n_e}, \\
& \boldsymbol{g}(\boldsymbol{x}, \hat{\boldsymbol{u}}^k, \boldsymbol{p}, t) \leq 0, \quad \forall t \in [t_0^k, t_\mathrm{f}^k],\ \forall k \in \overline{1, n_e}, \\
& \hat{\boldsymbol{u}}^k(t) \in [\hat{\boldsymbol{u}}^{k,L}(t), \hat{\boldsymbol{u}}^{k,U}(t)], \quad \forall k \in \overline{1, n_e}, \\
& \boldsymbol{p} \in [\boldsymbol{p}_\mathrm{min}, \boldsymbol{p}_\mathrm{max}].
\end{aligned}
\tag{3.37}
$$

where $\boldsymbol{y} = (\hat{\boldsymbol{x}}_0^1, \hat{\boldsymbol{x}}_0^2, \ldots, \hat{\boldsymbol{x}}_0^{n_e}, \hat{\boldsymbol{u}}^1, \hat{\boldsymbol{u}}^2, \ldots, \hat{\boldsymbol{u}}^{n_e}, \Delta t^1, \Delta t^2, \ldots, \Delta t^{n_e}, \boldsymbol{p})^T$ if we consider n_e PWC segments. The optimization algorithm presented earlier, for the case of CVP method,

applies here directly without any major change. The sequential integration of the set of ODEs (2.11) may have several distinct advantages. Numerical stability of integration of stiff systems may be dramatically improved. Moreover, such formulation allow to optimize dynamically unstable systems. Finally, such lifting approach (enlargement of decision variable space by addition of new variables) results in sparse NLP problems which can be in many cases resolved more efficiently than their condensed (dense) alternatives. These features make Direct Multiple Shooting to receive growing attention in the scientific and process engineering community.

3.4 Methods for Computing Gradients

The latter two direct methods of solving an OCP, we presented, require solving of NLP problems. This resolution requires gradient information with regard to dynamic system embedded in the problem.

According to Rosen and Luus (1991), these gradients can be deterministically computed by using of one of the following approaches

(i) Finite differences method

is based on integration of the system (2.10) repetitively with slightly changed (perturbed) value of one of the optimized parameters $\boldsymbol{y}$. The gradients to objective function can be then computed in the following way

$$\nabla_{y_i}\mathcal{J} = \frac{\mathcal{J}(y_{i-}, y_i + \Delta y_i) - \mathcal{J}(\boldsymbol{y})}{\Delta y_i}, \tag{3.38}$$

where $y_{i-} = (y_1, y_2, \ldots, y_{i-1}, y_{i+1}, \ldots, y_{n_y})$ and n_y denotes the number of optimized variables. Gradients to constraint functions can be derived similarly since we have shown (in Section 2.2) that any constraint can be rewritten into the form of objective criterion.

The advantage of this method lies in the fact that it does not require adding of any additional differential states or equations. On the other hand, the entire ODE system has to be integrated n_y times for each small perturbation of the parameter. Method of finite differences is generally very inaccurate but easily implementable and can be used in combination with other gradient methods in order to improve supplied gradient information accuracy.

(ii) Sensitivity equations method

is mainly used for problems embedded with possibly large number of differential equations but preferably small number of parameters. The gradients of objective function are computed as

$$\frac{\partial \mathcal{J}}{\partial y_i} = \frac{\partial \mathcal{G}}{\partial \boldsymbol{x}}\bigg|_{t_\mathrm{f}} \frac{\partial \boldsymbol{x}}{\partial y_i} + \frac{\partial \mathcal{G}}{\partial \boldsymbol{p}} \frac{\partial \boldsymbol{p}}{\partial y_i} + \int_{t_0}^{t_\mathrm{f}} \frac{\partial \mathcal{F}}{\partial \boldsymbol{x}} \frac{\partial \boldsymbol{x}}{\partial y_i} + \frac{\partial \mathcal{F}}{\partial \boldsymbol{u}} \frac{\partial \boldsymbol{u}}{\partial y_i} + \frac{\partial \mathcal{F}}{\partial \boldsymbol{p}} \frac{\partial \boldsymbol{p}}{\partial y_i} \,\mathrm{d}t, \tag{3.39}$$

where parametric sensitivities $\partial \boldsymbol{x}/\partial y_i$ are computed from

$$\frac{\mathrm{d}}{\mathrm{d}t} \frac{\partial \boldsymbol{x}}{\partial y_i} = \frac{\partial \boldsymbol{f}}{\partial \boldsymbol{x}} \frac{\partial \boldsymbol{x}}{\partial y_i} + \frac{\partial \boldsymbol{f}}{\partial \boldsymbol{u}} \frac{\partial \boldsymbol{u}}{\partial y_i} + \frac{\partial \boldsymbol{f}}{\partial \boldsymbol{p}} \frac{\partial \boldsymbol{p}}{\partial y_i}, \qquad \frac{\partial \boldsymbol{x}}{\partial y_i}\bigg|_{t_0} = \frac{\partial \boldsymbol{x}_0}{\partial \boldsymbol{p}} \frac{\partial \boldsymbol{p}}{\partial y_i}. \tag{3.40}$$

This method thus requires solving of additional $(n_x \times n_p)$ differential equations. The main disadvantage of sensitivity equations method then lies in creation of a large system of differential equations because for each optimized parameter a new set of n_x sensitivity equations is added. The number of additional ODEs is, however, not affected by the number of constraints associated with the optimization problem and this is why the usage of sensitivity equations method is convenient for problems with large number of constraints.

(iii) Adjoint variables method

exploits the properties of NCO and adjoint variables, previously described in Section 3.1. It can be effectively used for systems with rather small number of constraints and large number of parameters. The gradients of objective function are computed this way

$$\begin{aligned}
\frac{\partial \mathcal{J}}{\partial t_\mathrm{f}} &= \frac{\partial \mathcal{G}}{\partial t_\mathrm{f}} + H(t_\mathrm{f}), \\
\frac{\partial \mathcal{J}}{\partial t_i} &= \frac{\partial \mathcal{G}}{\partial t_i} + H(t_i^-) - H(t_i^+), \\
\frac{\partial \mathcal{J}}{\partial \boldsymbol{p}} &= \frac{\partial \mathcal{G}}{\partial \boldsymbol{p}} - \mathcal{J}_p(t_0) + \frac{\partial \boldsymbol{x}_0^T}{\partial \boldsymbol{p}} \boldsymbol{\lambda}(t_0), \\
\frac{\partial \mathcal{J}}{\partial \boldsymbol{u}^i} &= \mathcal{J}_u(t_{i-1}) - \mathcal{J}_u(t_i),
\end{aligned} \tag{3.41}$$

where

$$\dot{\mathcal{J}}_u = \frac{\partial H}{\partial \boldsymbol{u}}, \qquad \mathcal{J}_u(t_\mathrm{f}) = \mathbf{0}, \tag{3.42}$$

$$\dot{\mathcal{J}}_p = \frac{\partial H}{\partial \boldsymbol{p}}, \qquad \mathcal{J}_p(t_\mathrm{f}) = \mathbf{0}. \tag{3.43}$$

The number of additional ODEs which must be integrated backward in time is $(n_x \times n_c) + n_p + n_u$. Equations are integrated separately because the process model IVP is integrated forward while the system of adjoint variables and auxiliary variables is integrated backward in time. Thus this method requires more effort on implementation side than the previous ones.

Chapter 4

Membrane Processes

This chapter is devoted to present basic theory of membrane separation and some of well-established membrane processes. Majority of attention is dedicated to diafiltration processes.

Membrane processes are used in the context of filtration of liquid or gas mixtures and their purification. They find applications mainly in biotechnology, pharmaceutical, and food industry, where fairly high purity conditions for the final product are required or where the products can be degraded by purification (e.g. proteins) using any of the standard separation techniques (e.g. distillation). Current membrane technologies exploit a great variety of membrane processes. These involve processes based on membrane reactors, diafiltration, pervaporation, membrane distillation, electrodialysis, etc. Common feature of these processes is the employment of the membrane separation principle.

4.1 Membrane Separation

Filtration theory defines membrane to be a thin, film-like structure which stands in between two, usually fluid, phases and separates them. This structure is, however, at the same time made porous to allow for passage of some fluid from one side of the membrane to the other one. Thus, it can act as a selective barrier which can be used for separation of particles (or chemicals). It can prevent to pass the particles with size bigger than the pores of the membrane, traditionally referred as macro-solutes, and obviously it allows the particles with smaller size, typically denoted as micro-solutes, to get through (to permeate). This is a fundamental principle of all membrane separation processes which can be distinguished

by the actual type and pore sizes of a used membrane (Cheryan, 1998). This can be seen in Fig. 4.1 where we observe that for:

- microfiltration (MF) membrane
  - macro-solutes are represented by suspended particles and bacteria bodies
  - micro-solutes are represented by macromolecules and species with smaller particle sizes
- ultrafiltration (UF) membrane
  - macro-solutes represent macromolecules (typically proteins) and species with larger particle sizes
  - micro-solutes represent dissociated acids, divalent salts, sugars, and species with smaller particle sizes
- nanofiltration (NF) membrane
  - dissociated acids, divalent salts, sugars, and species with larger particle sizes are retained by the membrane
  - undissociated acids and monovalent salts can be pass through the membrane
- reverse osmosis (RO) membrane
  - only water passes through membrane and thus term macro-solutes stands for any other species in solution

This classification considers only filtration of liquid solutions since gas separation is out of the scope of this study.

Membrane separation is an external force driven process. This force may be applied in form of increased/decreased transmembrane pressure (that is the most common case), increased/decreased temperature (e.g. membrane distillation) or by electric field (electrodialysis).

There are two main ways of filtering a feed solution through the membrane, dead-end and cross-flow filtration. In dead-end filtration, treated solution is present on one side of the membrane at the beginning of the operation. Then, certain amount of force (usually increased pressure) is applied to enforce the filtration. This is done until some

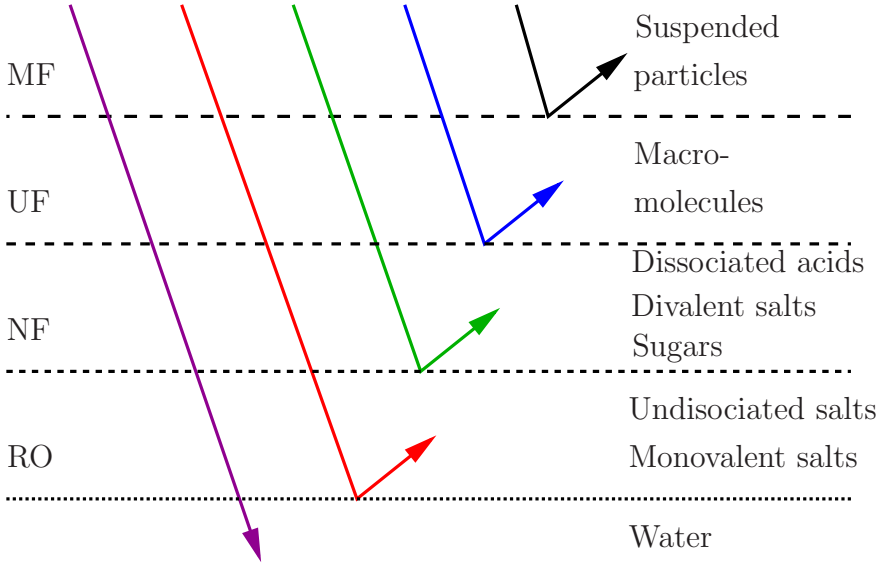


Figure 4.1: Classification of membranes with regard to pore size and filterable/retained components.

required concentration of micro- or macro-solute is achieved. Then, it is usually necessary to remove a filtration cake (i.e. accumulated matter) consisting of retained macro-solute and the membrane is prepared for another operation (batch).

In cross-flow filtration, solution is continuously transfered to the membrane module which is usually a tube with membrane on the inner side. The term "cross-flow" is used since the permeate (stream that passes through the membrane) flows perpendicularly to the feed stream. Unlike dead-end filtration, this setup is obviously suitable for both continuous and discontinuous (batch) treatment of solutions.

4.2 Modeling of Membrane Processes

In the last century, many theories have been developed and presented to describe the complex phenomena happening in the system: solution – membrane – permeate. The most evolved theoretical concept is using classical (stagnant) film theory (Zydney, 1997) which predicts a flow through ultrafiltration membrane (flux, q) to be given by

$$q = k \ln \frac{c_{\text{lim}}}{c_1}, \tag{4.1}$$

where k is mass transfer coefficient, c_1 is macro-solute concentration in the feed stream and c_{lim} represent limiting concentration of macro-solute. Term "limiting concentration" basically stands for the maximal concentration of macro-solute that can be attained in the system. Note that once this concentration is reached, the flux is zero. Historically, c_{lim} has been denoted as wall concentration c_{w} or gel concentration c_{g} to express the phenomena which cause such effects. Practical filtrations, however, did not follow such behavior of the membranes in many cases and that is why terms such "limiting concentration" and "limiting flux" are being used today.

There are theoretical methods that enable for prediction of the values of mass transfer coefficient and limiting concentration of macrosolute. These are based on analysis of e.g. viscosity of the solution, flow regime (this applies for the case of cross-flow filtration), and osmotic phenomena. On the other hand, mathematical form of Eq. (4.1) makes it possible to identify k and c_{lim} using experimental measurements and linear regression. This can be seen if Eq.(4.1) is rewritten such that $-k$ is a slope of the affine function in $\ln c_1$ and $k \ln c_{\text{lim}}$ is y-intercept of this function.

Practical limitations of this model of membrane flux are evident. It considers k and c_{lim} to be constant and thus neglects any e.g. viscosity effects or transmembrane pressure changes. To overcome these issues, various analogies of Eq. (4.1) have been proposed (Aimar and Field, 1992; Mulder, 1996). There is also no exact theoretical approach for dealing with fouling phenomena connected to aging of the membrane and dynamical changes that vary membrane conformation and characteristics.

Another popular theoretical approach for modeling (RO, NF, UF, MF) membrane response is so-called osmotic pressure model. According to this model, membrane flux can be written as

$$q = \frac{\Delta P - \pi}{\mu R_m}, \tag{4.2}$$

where ΔP stands for transmembrane pressure, π denotes osmotic pressure, μ is solution viscosity, and R_m represents resistance of the membrane. This model became popular since it can be applied for the wide range of operational conditions (e.g. pressures). Moreover, its form can be explained very naturally, i.e. applied transmembrane pressure should overcome reversely-acting osmotic pressure. The inverse proportionality of flux versus viscosity and membrane resistance is also evident and logical.

On the other hand, both above mentioned type of models a priori assume that rejection of macro-solute by membrane is complete. The rejection of particular solute by membrane,

R_i, is defined by

$$R_i = 1 - \frac{c_{\mathrm{p}i}}{c_i}, \tag{4.3}$$

where i refers to the ith component of the solution ($i = 1$ for macro-solute, $i = 2$ for micro-solute) and c_{pi} denotes its concentration in the permeate. From the process point of view, it is obvious that in order to reach better separation performance, used membrane and designed operation conditions should be such that they imply maximal rejection of macro-solute (ideally $R_1 = 1$) and the lowest possible rejection of micro-solute (in ideal case $R_2 = 0$).

If the operational conditions, such as pressure, temperature, and hydrodynamic conditions are fixed, membrane rejection of particular species can in principle vary with varying concentrations in the system. The same concept applies for modeling of membrane flux. It is then usually preferred to model membrane behavior (permeation/retention response to various concentrations) by fitting of experimental data to arbitrarily (but conveniently) chosen linear or non-linear mathematical model (Caoa and Henson, 2003; Chatterjee et al., 2004). Such form of the model is unlike to directly interpret natural phenomena but provides very good alternative in situations where there are no practically applicable theoretical models to predict complex membrane response (flux and rejection).

4.3 Diafiltration Process

Diafiltration is known as an effective membrane process for separation of two or more solutes from a solution. Currently, it is well established in chemical, biochemical, food and pharmaceutical industries (Lipnizki et al., 2002). Its aim is the increase of concentration of a desired product together with the simultaneous decrease of concentration of impurities in solution. It was described as "Killing two birds with one stone" method in Jönsson and Trägårdh (1990).

Some of the most important applications in this field include antigen purification (Schu and Mitra, 2001), fractionation of whey protein isolate (Cheang and Zydney, 2004), albumin production from human blood plasma for medical use (Jaffrin and Charrier, 1994) and recovery of animal blood proteins from slaughterhouse effluents (Belhocine et al., 1998), separation of protease from tuna spleen extract (Li et al., 2006), recovery of β-galactosidase from PEG-rich top-phase of fermentation broth extract (Veide et al., 1989), production of

recombinant DNA derived human protein pharmaceuticals (van Reis et al., 1997) and antibody preparation (Luo et al., 2004), purification of soybean lecithin (Basso et al., 2009) and leaf proteins (Dutré et al., 1994), or concentration and desalination of gelatin (Simon et al., 2002).

Diafiltration process may be implemented as continuous or discontinuous (batch) while the current setup is case-by-case dependent on the scale, physical properties of the system (e.g. solution viscosity and stability), and overall economics.

This work deals with the discontinuous application of diafiltration. In comparison with continuous processes, batch operations allow to use membranes with reduced area in order to reach the target product quality, that usually leads to smaller space requirement and lower investment costs (Lipnizki et al., 2002). Moreover, batch processing is particularly suited for applications where the process liqueur is manufactured in batches or lots before any subsequent separation is undertaken.

A schematic diagram of a discontinuous membrane diafiltration process is shown in Figure 4.2.

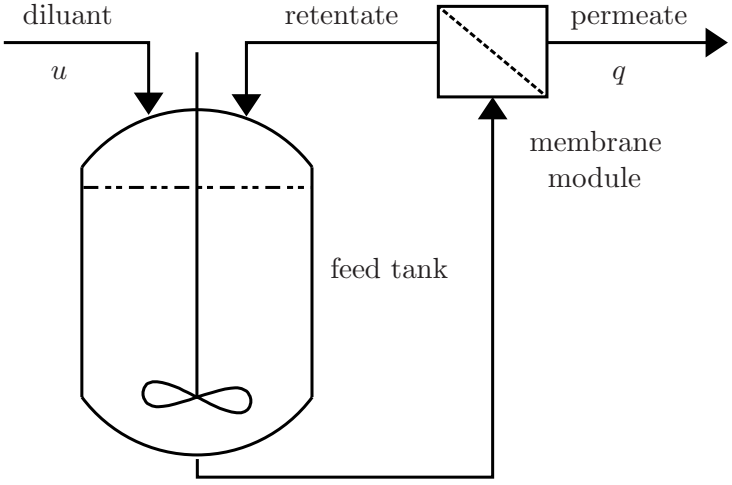


Figure 4.2: Schematic representation of a generalized batch diafiltration process.

Considering a process liqueur with two solutes, the general purpose of such batch plant can be summarized as to increase the macro-solute concentration from $c_{1,0}$ to $c_{1,\mathrm{f}}$ and to reduce the micro-solute concentration from $c_{2,0}$ to $c_{2,\mathrm{f}}$. The fractionation is accomplished by performing a so called *diafiltration* mode in which the micro-solute is washed out of the process liqueur by introducing fresh buffer (i.e. diluant), of certain flowrate $u(t)$, into

the feed reservoir while simultaneously removing the permeate with very low macro-solute content.

Most diafiltration processes operate with constant transmembrane pressure that is achieved by simply adjusting the pressure with the retentate valve. We note here that other types of process control strategies, such as constant flux or constant wall concentration control, are also implemented in engineering practice. These are normally preferred when unfavorable effects such as enhanced fouling or product quality deterioration are associated with high concentration of retained species at the membrane wall. For instance, when animal cell damage (Maiorella et al., 1991) or denaturation/adsorption of high-value protein pharmaceuticals (van Reis et al., 1997) are of major concern. The work presented here examines the constant pressure approach.

4.3.1 Process Model

We consider a membrane filtration plant (for RO, UF, NF, or MF) with a given membrane area that operates under fixed operating conditions. The studied filtration system applies a cross-flow and pressure setpoint, and the permeate flows uncontrolled out of the membrane module. We assume that the system is well-mixed, and the introduction of diluant causes no local concentration differences. The balance of each solute can be written as

$$\frac{\mathrm{d}c_i}{\mathrm{d}t} = \frac{c_i q}{V}(R_i - \alpha), \quad c_i(t_0) = c_{i0}, \quad i = 1, 2 \tag{4.4}$$

where V is the retentate volume at time t. The rejection coefficient $R_i(c_1, c_2)$ is assumed to be a function of both concentrations. The same holds for the permeate flowrate $q(c_1, c_2)$. Variable $\alpha(t)$ is a dimensionless variable which is defined as a fraction between diluant flowrate and flux

$$\alpha(t) = \frac{u(t)}{q(t)}. \tag{4.5}$$

The volume balance can be written as

$$\frac{\mathrm{d}V}{\mathrm{d}t} = (\alpha - 1)q, \quad V(t_0) = V_0. \tag{4.6}$$

Note that the time-dependent variables (i.e. permeate flux and the solute rejections) are solely a functions of feed concentrations in the process model. Thus according to our previous assumptions, the model in its current form does not encounter changes in process parameters (pressure, temperature, hydrodynamic conditions, etc.) that might influence

the membrane response during the process run. Furthermore, the model is limited to applications where fouling is not pronounced. This means that the findings are restricted to applications where (i) fouling does not occur, (ii) the impact of fouling on flux is sufficiently less than the impact induced by changes in feed composition, or (iii) fouling occurs rapidly within the time-scale of the entire process, and Eqs. (4.4) and (4.6) representing the fouled membrane are given.

4.3.2 Operational Modes of Diafiltration

Choosing the right diluant utilization strategy is a critical aspect to consider in diafiltration process control. Batch processing can be performed in different ways depending on how the addition of the diluant (diafiltration or washing solvent) into the feed tank is scheduled. The standard way of reaching the dual objective of fractionation and concentration is to

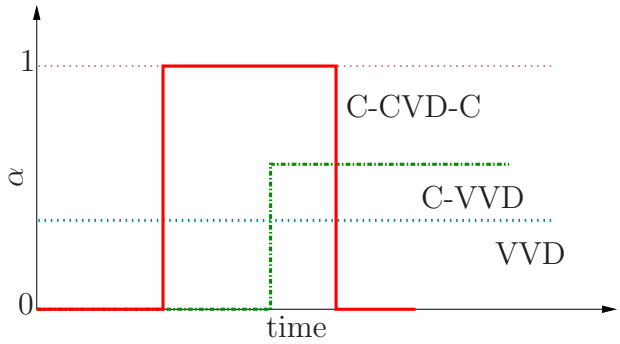


Figure 4.3: Representation of classical three-step processing (C-CVD-C), pre-concentration combined with variable-volume diafiltration (C-VVD), and variable-volume diafiltration (VVD) operation in terms of the α function.

perform a multi-step process including pre-concentration (C), constant-volume diafiltration (CVD), and post-concentration steps. Other strategies include variable-volume diafiltration (VVD) Jaffrin and Charrier (1994), or a variation of it, pre-concentration followed by variable-volume diafiltration (C-VVD) Foley (2006). These processes are best described with α (i.e. the ratio of diluant flow to permeate flow) as a function of operation time as shown in Figure 4.3.

Once we are concerned with optimal performance of a diafiltration, it has been pointed out in Fikar et al. (2010) that the best time-varying profile of the diluant addition needs not necessarily be one of the pre-defined profiles depicted in Figure 4.3. The optimal control

trajectory of $\alpha(t)$ (or equivalently the diluant flow) can be determined by formulating an optimization problem subject to process model described by a set of differential equations. The diafiltration process, that is designed by the evaluation of the optimal time-varying profile of the diluant flow, has been then referred to as dynamic-volume diafiltration (DVD).

4.3.3 Optimization of Diafiltration Process

The wash-water utilization strategy of DVD may differ from conventional diafiltration processes. However, in many cases it may be attractive to implement the optimal trajectory since it can lead to reduced operation time, diluant consumption, and product losses. The diluant consumption and operation time minimizations are generally of major concern.

Batch production takes place periodically; when the production is complete, the plant and equipment are available for the next batch. Processing time is then a key factor to increase production throughput. Moreover, diafiltration is commonly associated with high consumption of diafiltration solvent. This liquid is commonly water with strict quality requirements regarding bacteriological contamination and organic/inorganic solute content (Madsen, 2001). Thus, the production of diafiltration liquid can contribute significantly to the overall operating costs of the plant.

As far as time minimization problem considered, it has been previously demonstrated that optimum diafiltration strategy can be found for filtration processes operating in discontinuous manner. The patent by Lutz (1997) provides an implementation procedure and a general formula for determining the optimal diafiltration path using idea of maximization of mass flux of permeable component through the membrane. Despite that this approach provides certain level of intuition and insight on time-optimal filtration control, its extendability onto different optimization tasks and more complex process setups is questionable.

Next, we introduce mathematical definitions of above mentioned process optimization problems. In the first one, minimum time problem, optimal trajectory of function $\alpha(t)$ is computed in order to minimize running time of batch diafiltration process. The second considers minimization of diluant consumption during the diafiltration process. Both of these problems involve, of course, restrictions to achieving given separation goal, i.e. driving the concentrations from initial to final state.

Minimum Time Problem

Mathematical formulation of this OCP is as follows

$$\mathcal{J}_1 = \min_{\alpha(t)} t_\mathrm{f} = \min_{\alpha(t)} \int_{t_0}^{t_\mathrm{f}} 1 \,\mathrm{d}t. \tag{4.7a}$$

s.t.

$$\dot{c}_1 = \frac{c_1 q}{V}(R_1 - \alpha), \qquad c_1(t_0) = c_{1,0}, \qquad c_1(t_\mathrm{f}) = c_{1,\mathrm{f}}, \tag{4.7b}$$

$$\dot{c}_2 = \frac{c_2 q}{V}(R_2 - \alpha), \qquad c_2(t_0) = c_{2,0}, \qquad c_2(t_\mathrm{f}) = c_{2,\mathrm{f}}, \tag{4.7c}$$

$$\dot{V} = (\alpha - 1)q, \qquad V(t_0) = V_0, \tag{4.7d}$$

$$\alpha \in [\alpha_\mathrm{min}, \alpha_\mathrm{max}], \tag{4.7e}$$

where α_min and α_max represent lower and upper constraints on the value of α respectively. Lower bound, α_min, obviously stands for pre/post-concentration mode when $\alpha = 0$. Value of upper constraint, α_max, may vary from one application to another.

Some applications require that α does not overcome 1. Other ones do not impose any upper bound on the value of α which in principle means that $\alpha_\mathrm{max} = \infty$. This can have a special meaning if it happens at the beginning or at the end of the operation. We will speak about a pure dilution mode where a certain volume of diluant is added into the system instantaneously. This can happen in a separate equipment not related to membrane equipment.

Minimum Diluant Problem

The second problem addresses minimization of total amount of diluant, $u(t) = \alpha(t)q(t)$, used to drive the process from initial state to a prescribed terminal state assuming that the final time t_f is a free variable. Mathematical formulation (4.7) remains unchanged in this case except for the cost function

$$\mathcal{J}_2 = \min_{\alpha(t)} \int_{t_0}^{t_\mathrm{f}} \alpha(t)q(t) \,\mathrm{d}t. \tag{4.8}$$

In both optimization problems, a special input-affine structure can be immediately recognized (control variable α enters linearly both problems, (4.7) and (4.8)). Recalling statements of previous chapter, it is convenient to approach the finding of optimal α using analytical Pontryagin's minimum principle.

Part II

Applications

Chapter 5

Optimal Operation of Diafiltration Processes

Optimal operation of batch diafiltration processes may be found by using of numerical techniques such as orthogonal collocation (as showed in Fikar et al. (2010)) or control vector parameterization (used in Paulen et al. (2011a)). In Paulen et al. (2012), we showed how analytical approach of dynamic optimization may be used either to solve or to simplify the problem. Most of the material presented in this chapter has been published in Paulen et al. (2012).

We make use of Pontryagin's minimum principle (Bryson, Jr. and Ho, 1975; Pontryagin et al., 1962) in order to solve the optimization problems (4.7) and (4.8) specified in previous chapter and in order to find the optimal operation of generalized batch diafiltration process. We may follow the procedure stated for control affine OCP in Example 2 in section 3.2.3.

Considering TPBVP (4.7b)–(4.7d) with state vector $\boldsymbol{x} = (c_1, c_2, V)^T$ and scalar control α, we can write necessary conditions for optimality as derived in Pontryagin's minimum principle

$$\alpha^* = \arg \min_{\alpha \in [\alpha_{\min}, \alpha_{\max}]} H(\boldsymbol{x}, \boldsymbol{\lambda}, \alpha) \equiv \arg \min_{\alpha \in [\alpha_{\min}, \alpha_{\max}]} \left\{ H_0(\boldsymbol{x}, \boldsymbol{\lambda}) + H_\alpha(\boldsymbol{x}, \boldsymbol{\lambda})\alpha \right\}, \tag{5.1a}$$

$$\dot{\boldsymbol{x}} = \frac{\partial H}{\partial \boldsymbol{\lambda}}, \quad \boldsymbol{x}(t_0) = \boldsymbol{x}_0, \quad \boldsymbol{x}(t_\mathrm{f}) = \boldsymbol{x}_\mathrm{f}, \tag{5.1b}$$

$$\dot{\boldsymbol{\lambda}} = -\frac{\partial H}{\partial \boldsymbol{x}}, \tag{5.1c}$$

$$H = 0, \quad \forall t \in [t_0, t_\mathrm{f}]. \tag{5.1d}$$

The last condition arises because of the synergy of two facts: optimal Hamiltonian is constant over the whole time horizon since it is not an explicit function of time and it

is zero at final time since the final time is free in all treated optimization problems (see Eq. (3.8e)).

The Hamiltonian is linear in α. Thus, its minimum will be attained with α^* being either on its boundaries or singular such as

$$\alpha^* = \begin{cases} \alpha_{\min} & \text{if } H_\alpha > 0, \\ \alpha_{\max} & \text{if } H_\alpha < 0, \\ \alpha_{\text{sing}} & \text{if } H_\alpha = 0. \end{cases} \tag{5.2}$$

In case of $H_\alpha = 0$ the Hamiltonian is singular and does not depend on α. According to Johnson and Gibson (1963) and Srinivasan et al. (2003), it may be possible to construct optimal (singular) surface $S(\boldsymbol{x}) = 0$ corresponding to singular control that depends on state variables only. Once $S(\boldsymbol{x}) = 0$ is known, we have all necessary information to switch between control arcs.

We use the fact that the condition $H_\alpha = 0$ implies (because of (5.1d)) that $H_0 = 0$ and also their derivatives w.r.t. time are equal to zero as well. We will make use of the following equations

$$H_0(\boldsymbol{x}, \boldsymbol{\lambda}) = 0, \tag{5.3a}$$

$$H_\alpha(\boldsymbol{x}, \boldsymbol{\lambda}) = 0, \tag{5.3b}$$

$$\frac{\mathrm{d}^i H_0}{\mathrm{d}t^i}(\boldsymbol{x}, \boldsymbol{\lambda}, \alpha) = 0, \tag{5.3c}$$

$$\frac{\mathrm{d}^i H_\alpha}{\mathrm{d}t^i}(\boldsymbol{x}, \boldsymbol{\lambda}, \alpha) = 0, \tag{5.3d}$$

to eliminate the adjoint variables $\boldsymbol{\lambda} = (\lambda_1, \lambda_2, \lambda_3)^T$ where ith order time derivatives will be considered with $i \in \{1, 2, \ldots\}$ taking the necessary value. We note that it is not possible to use both conditions (5.3c) and (5.3d) simultaneously since they are linearly dependent on each other and thus contain the same information about singular arc. This can be shown for $i = 1$ using (5.1d) and its time derivative

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{\mathrm{d}H_0}{\mathrm{d}t} + \frac{\mathrm{d}H_\alpha}{\mathrm{d}t}\alpha + H_\alpha \frac{\mathrm{d}\alpha}{\mathrm{d}t} = 0. \tag{5.4}$$

Since term $H_\alpha = 0$ it is clear that $\dot{H}_0$ and $\dot{H}_\alpha$ may not vary independently so zeroing one of these terms zeroes the other as well. This applies analogically for $i > 1$.

5.1 Minimum Time Problem

The Hamiltonian function for the studied problem is of the form

$$H = 1 + \lambda_1 \frac{c_1 q}{V}(R_1 - \alpha) + \lambda_2 \frac{c_2 q}{V}(R_2 - \alpha) + \lambda_3(\alpha - 1)q \tag{5.5a}$$

$$= \alpha \frac{q}{V}(-\lambda_1 c_1 - \lambda_2 c_2 + \lambda_3 V) + \frac{q}{V}(\lambda_1 c_1 R_1 + \lambda_2 c_2 R_2 - \lambda_3 V) + 1, \tag{5.5b}$$

and the adjoint variables are defined by the following differential equations

$$\begin{aligned}\dot{\lambda}_1 =& -\lambda_1 \frac{1}{V}[(q + c_1 q_1)(R_1 - \alpha) + c_1 q R_{11}] \\ & - \lambda_2 \frac{1}{V}[c_2 q_1 (R_2 - \alpha) + c_2 q R_{21}] - \lambda_3(\alpha - 1)q_1,\end{aligned} \tag{5.6a}$$

$$\begin{aligned}\dot{\lambda}_2 =& -\lambda_1 \frac{1}{V}[c_1 q_2 (R_1 - \alpha) + c_1 q R_{12}] \\ & - \lambda_2 \frac{1}{V}[(q + c_2 q_2)(R_2 - \alpha) + c_2 q R_{22}] - \lambda_3(\alpha - 1)q_2,\end{aligned} \tag{5.6b}$$

$$\dot{\lambda}_3 = \frac{q}{V^2}[\lambda_1 c_1 (R_1 - \alpha) + \lambda_2 c_2 (R_2 - \alpha)], \tag{5.6c}$$

where

$$q_1 = \frac{\partial q}{\partial c_1}, \qquad R_{11} = \frac{\partial R_1}{\partial c_1}, \qquad R_{21} = \frac{\partial R_2}{\partial c_1}, \tag{5.7a}$$

$$q_2 = \frac{\partial q}{\partial c_2}, \qquad R_{12} = \frac{\partial R_1}{\partial c_2}, \qquad R_{22} = \frac{\partial R_2}{\partial c_2}. \tag{5.7b}$$

The optimality conditions (5.3) are as follows

$$H_\alpha : \ -\lambda_1 c_1 - \lambda_2 c_2 + \lambda_3 V = 0, \tag{5.8a}$$

$$H_0 : \ \lambda_1 c_1 R_1 q + \lambda_2 c_2 R_2 q - \lambda_3 V q + V = 0, \tag{5.8b}$$

$$\frac{\mathrm{d}H_\alpha}{\mathrm{d}t} : \ \lambda_1 c_1 p_1(c_1, c_2) + \lambda_2 c_2 p_2(c_1, c_2) + \lambda_3 V p_3(c_1, c_2) = 0, \tag{5.8c}$$

where

$$p_i(c_1, c_2) = R_i(q + c_1 q_1 + c_2 q_2) + q(c_1 R_{i1} + c_2 R_{i2}) \quad i = 1, 2 \tag{5.9a}$$

$$p_3(c_1, c_2) = -(q + c_1 q_1 + c_2 q_2). \tag{5.9b}$$

For the next step, we use equations (5.8a) and (5.8c) which let us, after some manipulations, arrive at condition

$$S = \lambda_1 c_1 S_1 + \lambda_2 c_2 S_2 = 0, \tag{5.10}$$

where S_1 and S_2 are given as

$$S_1(c_1, c_2) = (R_1 - 1)(q + c_1 q_1 + c_2 q_2) + q(c_1 R_{11} + c_2 R_{12}), \tag{5.11a}$$

$$S_2(c_1, c_2) = (R_2 - 1)(q + c_1 q_1 + c_2 q_2) + q(c_1 R_{21} + c_2 R_{22}). \tag{5.11b}$$

Since (5.10) depends on unknown trajectories of adjoint variables it might be in general very difficult (maybe even impossible) to find concentration trajectory along which this equation is satisfied. However, there are some cases when it will be easily satisfied:

- $R_1 = 1$ ($R_{11} = R_{12} = 0$). This represents a common situation for a macro-solute that does not get through the membrane and micro-solute can have arbitrary properties. The optimal curve is given as

$$S(c_1, c_2) = (R_2 - 1)(q + c_1 q_1 + c_2 q_2) + q(c_1 R_{21} + c_2 R_{22}) = 0, \tag{5.12}$$

- both $R_1 \leq 1, R_2$ are constant ($R_{ij} = 0$). If both retention coefficients R_1 and R_2 are constant and do not depend on concentrations (for example a perfect membrane with $R_1 = 1$, $R_2 = 0$) the optimal curve is given as

$$S(c_1, c_2) = q + c_1 q_1 + c_2 q_2 = 0. \tag{5.13}$$

We will further differentiate w.r.t. time the equation (5.10) (note that this is equivalent to taking the second order time derivative of (5.3b)). This differentiation yields

$$\lambda_1 c_1 (a_1 \alpha + b_1) + \lambda_2 c_2 (a_2 \alpha + b_2) + \lambda_3 V b_3 = 0, \tag{5.14}$$

where expressions a_i and b_i for $i = 1, 2$ are given as follows

$$a_i = -c_1 q \frac{\partial S_i}{\partial c_1} - c_2 q \frac{\partial S_i}{\partial c_2}, \tag{5.15a}$$

$$b_i = c_1 \left(q R_1 \frac{\partial S_i}{\partial c_1} - (q R_{i1} + R_i q_1) S_1 \right) + c_2 \left(q R_2 \frac{\partial S_i}{\partial c_2} - (q R_{i2} + R_i q_2) S_2 \right), \tag{5.15b}$$

and

$$b_3 = c_1 q_1 S_1 + c_2 q_2 S_2. \tag{5.15c}$$

By writing equations (5.8a), (5.8c) and (5.14) together we recognize homogeneous system of linear equations in variables $\lambda_1 c_1$, $\lambda_2 c_2$ and $\lambda_3 V$. Such a system possesses a non-trivial solution only if determinant of its coefficient matrix is equal to zero. Using this and

after some rearrangement we arrive at expression for singular optimal control

$$\begin{vmatrix} 1 & 1 & -1 \\ S_1 & S_2 & 0 \\ a_1\alpha + b_1 & a_2\alpha + b_2 & b_3 \end{vmatrix} = 0 \;\Rightarrow\; \alpha_{\text{sing}} = \frac{(S_1 - S_2)b_3 + S_1 b_2 - S_2 b_1}{S_2 a_1 - S_1 a_2}. \tag{5.16}$$

5.2 Minimum Diluant Problem

The Hamiltonian function for the diluant problem is of the form

$$H = \alpha q + \lambda_1 \frac{c_1 q}{V}(R_1 - \alpha) + \lambda_2 \frac{c_2 q}{V}(R_2 - \alpha) + \lambda_3(\alpha - 1)q \tag{5.17a}$$

$$= \alpha \frac{q}{V}(-\lambda_1 c_1 - \lambda_2 c_2 + \lambda_3 V + V) + \frac{q}{V}(\lambda_1 c_1 R_1 + \lambda_2 c_2 R_2 - \lambda_3 V), \tag{5.17b}$$

where the adjoint variables are defined by the following differential equations

$$\begin{aligned} \dot{\lambda}_1 =& -\alpha q_1 - \lambda_1 \frac{1}{V}[(q + c_1 q_1)(R_1 - \alpha) + c_1 q R_{11}] \\ & - \lambda_2 c_2 \frac{1}{V}[q_1(R_2 - \alpha) + q R_{21}] - \lambda_3(\alpha - 1)q_1, \end{aligned} \tag{5.18a}$$

$$\begin{aligned} \dot{\lambda}_2 =& -\alpha q_2 - \lambda_1 c_1 \frac{1}{V}[q_2(R_1 - \alpha) + q R_{12}] \\ & - \lambda_2 \frac{1}{V}[(q + c_2 q_2)(R_2 - \alpha) + c_2 q R_{22}] - \lambda_3(\alpha - 1)q_2, \end{aligned} \tag{5.18b}$$

$$\dot{\lambda}_3 = \frac{q}{V^2}[\lambda_1 c_1(R_1 - \alpha) + \lambda_2 c_2(R_2 - \alpha)], \tag{5.18c}$$

and variables q_i, R_{ij} are defined in (5.7). The optimality conditions (5.3) are as follows

$$H_\alpha : \; -\lambda_1 c_1 - \lambda_2 c_2 + \lambda_3 V + V = 0, \tag{5.19a}$$

$$H_0 : \lambda_1 c_1 R_1 + \lambda_2 c_2 R_2 - \lambda_3 V = 0, \tag{5.19b}$$

$$\frac{\mathrm{d}H_0}{\mathrm{d}t} : \lambda_1 c_1 m_1(c_1, c_2) + \lambda_2 c_2 m_2(c_1, c_2) - \lambda_3 V = 0, \tag{5.19c}$$

where

$$m_1(c_1, c_2) = 1 - c_1 R_{11} - c_2 R_{12}, \tag{5.20a}$$

$$m_2(c_1, c_2) = 1 - c_1 R_{21} - c_2 R_{22}. \tag{5.20b}$$

Using equations (5.19b) and (5.19c) we can arrive at condition

$$S = \lambda_1 c_1 S_1 + \lambda_2 c_2 S_2 = 0, \tag{5.21}$$

where $S_1 = R_1 - m_1$ and $S_2 = R_2 - m_2$. Again, validity of this equation depends on adjoint variables except for special cases:

- $R_1 = 1$ ($R_{11} = R_{12} = 0$). The optimal curve is given as

$$S(c_1, c_2) = R_2 - 1 + c_1 R_{21} + c_2 R_{22} = 0, \tag{5.22}$$

- either R_1 or R_2 is constant. The optimal surface does not exist and the optimal control is of bang-bang type.

Further we choose system of three linearly independent homogeneous equations (5.19b), (5.19c) and time derivative of (5.21) to form a coefficient matrix. Its determinant gives the condition for optimal control along singular arc

$$\alpha_{\text{sing}} = \frac{b_2 S_1 - b_1 S_2}{a_1 S_2 - a_2 S_1}, \tag{5.23}$$

where

$$a_i = -c_1 \frac{\partial S_i}{\partial c_1} - c_2 \frac{\partial S_i}{\partial c_2}, \tag{5.24a}$$

$$b_i = c_1 R_1 \frac{\partial S_i}{\partial c_1} + c_2 R_2 \frac{\partial S_i}{\partial c_2} - c_1 R_{i1} S_1 - c_2 R_{i2} S_2. \tag{5.24b}$$

5.3 Optimal Control in Special Cases

As it was shown, the optimal state surface is in special cases a function of concentrations only $S(c_1, c_2) = 0$. Thus, it is a curve in the concentration space. Once it is found, the corresponding singular control can be obtained by considering its derivative with respect to time

$$\frac{\mathrm{d}S(c_1, c_2)}{\mathrm{d}t} = \frac{\partial S}{\partial c_1}\dot{c}_1 + \frac{\partial S}{\partial c_2}\dot{c}_2 = 0. \tag{5.25}$$

Using process differential equations (4.4) then yields

$$\frac{\partial S}{\partial c_1}\frac{c_1 q}{V}(R_1 - \alpha_{\text{sing}}) + \frac{\partial S}{\partial c_2}\frac{c_2 q}{V}(R_2 - \alpha_{\text{sing}}) = 0. \tag{5.26}$$

This equation can be satisfied if α is calculated as

$$\alpha_{\text{sing}}(t) = \frac{\frac{\partial S}{\partial c_1} c_1 R_1 + \frac{\partial S}{\partial c_2} c_2 R_2}{\frac{\partial S}{\partial c_1} c_1 + \frac{\partial S}{\partial c_2} c_2}. \tag{5.27}$$

The overall optimal operation can be stated as follows:

1. The first step is either pure concentration ($\alpha = \alpha_{\min} = 0$) or operation with $\alpha = \alpha_{\max}$ until the condition $S(c_1, c_2) = 0$ is met.

2. The second step is filtration with time-dependent $\alpha_{\text{sing}}(c_1, c_2)$ given by (5.27) maintaining optimal concentration values.

3. Finally, the third step is again either pure concentration ($\alpha = 0$) or operation with $\alpha = \alpha_{\max}$ until final concentrations of both components are obtained.

Any of these three steps can be missing at a particular problem, depending on process initial and final conditions as well as actual functions $R_2(c_1, c_2)$, $q(c_1, c_2)$. For example, if condition $S(c_1, c_2)$ does not exist or it is not possible to satisfy it for particular process initial and final conditions, then the optimal control will be of bang-bang type (i.e. control will be saturated).

5.4 Optimal Control in General Case

In general it is not possible to end up with closed form representation of singular surface without using adjoint variables $\boldsymbol{\lambda}$ which trajectories are in our case not known and have to be found numerically case-by-case. On the other hand, as we have shown, it is possible to find an expression for singular control (see Eq. (5.16) and Eq. (5.23)) as a function of concentrations only.

The overall optimal control strategy will not change from the previously mentioned one. In this case, however, switches between constrained and singular control trajectories have to be found by other means. In this work we propose to find them numerically by formulating a simple NLP problem.

We form this NLP problem with five unknowns $\Delta t^1, \Delta t^2$, and Δt^3 being the lengths of time intervals of the respective phases and α^1 and α^3 being the constant values of α in the first and the third phase. Optimal value of α^1 and α^3 will either be on minimum or on maximum. In the second phase, optimal α will be given by (5.16) for the minimum time problem and by (5.23) for the minimum diluant problem. Numerical methods that can solve this NLP problem. Once it is solved numerically, we know all needed information about optimal operation to apply it to the process.

Chapter 6

Examples and Case Studies

In this section we determine the optimal control strategies where the permeate flux is given by some well-known models, including the limiting flux and osmotic pressure models. We then examine five case studies from the literature where the flux is predicted by empirical models specific to the system in question. Results presented in this section have been published in Paulen et al. (2011a,b, 2012).

6.1 Optimization at Limiting Flux

Let us consider a membrane plant that operates under limiting flux conditions (4.1) (i.e. the operation is performed in the pressure-independent flux regime under fixed hydrodynamic conditions). We assume that rejections are ideal ($R_1 = 1$, $R_2 = 0$) and that $\alpha_{\max} = \infty$. Different nomenclature and symbols have been in use in the literature for presenting Eq. (4.1) that is historically referred to as "gel polarization model". From the point of view of mathematical treatment, it is essentially the same diafiltration problem (provided by Eq. (4.1)-type formula) that has been the subject of experimental and theoretical investigations by many authors (e.g. in Field (2011); Ng et al. (1976); Paulen et al. (2011b); Yazdanshenas et al. (2005); Zydney (1997)).

The time-optimal control strategy defines the optimal concentration curve by (5.13) and it is a function of the macro-solute only

$$S(c_1) = q + c_1 \frac{\mathrm{d}q}{\mathrm{d}c_1} = 0. \tag{6.1}$$

This shows that optimal operation is obtained at a constant concentration which is from

the last equation derived as

$$c_1 = \frac{c_{\text{lim}}}{\text{e}}. \tag{6.2}$$

Macro-solute concentration stays on its optimal value if the control is calculated from (5.27)

$$\alpha_{\text{sing}}(t) = \frac{\frac{\partial S}{\partial c_1} c_1}{\frac{\partial S}{\partial c_1} c_1} = 1. \tag{6.3}$$

Hence the singular control is given by CVD operation. Using this information one can form following three-step procedure for optimal operation:

- First step:

$$\alpha^* = \begin{cases} 0 & \text{if } c_{1,0} < c_{\text{lim}}/\text{e}, \\ \infty & \text{if } c_{1,0} > c_{\text{lim}}/\text{e}. \end{cases} \tag{6.4}$$

  We note here that in practice it is usually the case that first condition holds and thus optimal operation is nearly always started with concentration step.

- Second step:

$$\alpha^* = 1 \quad \text{for } c_1 = c_{\text{lim}}/\text{e}. \tag{6.5}$$

- Third step:

$$\alpha^* = \begin{cases} 0 & \text{if } c_{1,\text{f}} > c_{\text{lim}}/\text{e},\ c_2 = c_{2.\text{f}}, \\ \infty & \text{if } c_{1,\text{f}} < c_{\text{lim}}/\text{e},\ c_2 = \frac{c_{2,\text{f}}}{c_{1,\text{f}}} c_{\text{lim}}/\text{e}, \end{cases} \tag{6.6}$$

  Additional conditions for concentration c_2 are considered to determine the switching time to commence this operation. In the first case, we switch to concentration mode ($\alpha = 0$) when the required concentration of micro-solute is reached (i.e. we disposed of specified amount of impurities). Switching to dilution mode ($\alpha = \infty$) in the second case is done such that the ratio of concentrations of both components is the same as final one. Dilution operation then keeps this ratio constant. Both final operations are then ended once the requirements for final product are satisfied.

Hence that optimal operation is defined in a form of feedback law and it depends, in majority of the cases, only on the final condition for c_1. In practice, we may distinguish three cases:

- $c_{1,f} > c_{\text{lim}}/\text{e}$

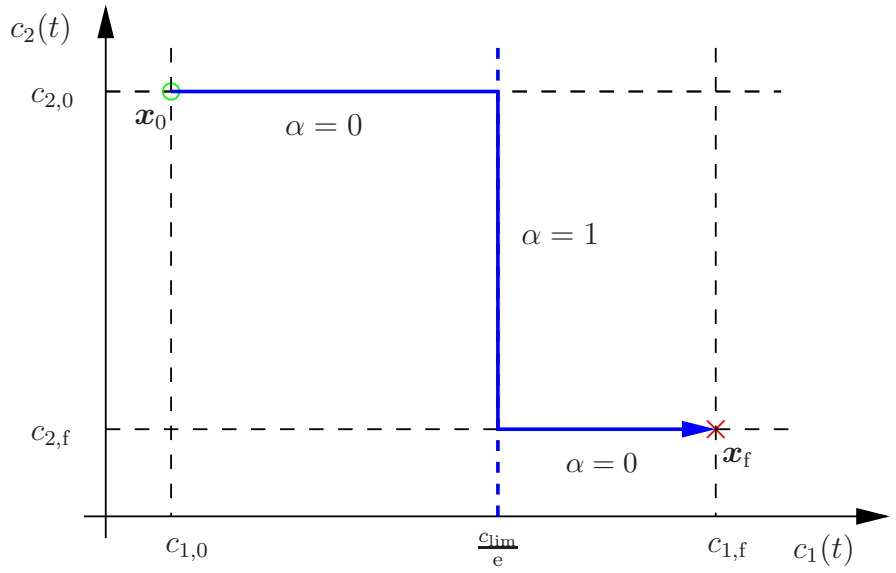


Figure 6.1: Optimal operation of diafiltration with limiting flux model in concentration diagram. Case of $c_{1,f} > c_{\mathrm{lim}}/\mathrm{e}$.

In this case the optimal operation is represented by the sequence $\alpha^* = \{0, 1, 0\}$, i.e. concentration step is performed first, then it is followed by CVD step, and finishes with another concentration step. This is shown in Fig. 6.1. Note that this case corresponds to the classic scenario considered by Ng et al. (1976) and the resulting optimal operation is the same as traditional C-CVD-C.

- $c_{1,f} < c_{\mathrm{lim}}/\mathrm{e}$

  Optimal operation is three step strategy $\alpha^* = \{0, 1, \infty\}$. We use concentration step followed by CVD ($\alpha = 1$) which continues until the concentration ratio of macro-solute to micro-solute reaches the final desired ratio. In the third step, the volume is increased by adding the correct amount of diluant instantaneously. The corresponding representation of this strategy is depicted in Fig. 6.2 using state (concentration) diagram. In this case none of the traditional control approaches is going to be optimal.

- $c_{1,f} = c_{\mathrm{lim}}/\mathrm{e}$

  This situation represents a special case which results in two-step optimal operation with $\alpha^* = \{0, 1\}$ performing a complete concentration step first and then reaching desired final state $\boldsymbol{x}_\mathrm{f}$ in CVD step.

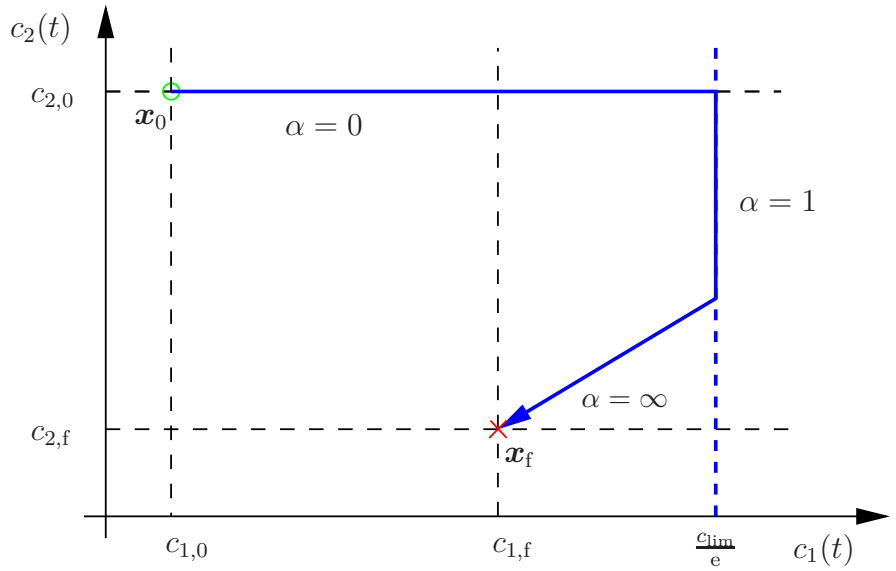


Figure 6.2: Optimal operation of diafiltration with limiting flux model in concentration diagram. Case of $c_{1,f} < c_{\mathrm{lim}}/\mathrm{e}$.

If the minimum diluant problem is considered, the optimal curve does not exist and optimal operation will consist of concentration step followed by pure dilution, $\alpha^* = \{0, \infty\}$.

Here it is implicitly assumed that the actual concentration stays below c_{lim} during the concentration step. If the limit case with $c_1 = c_{\mathrm{lim}}$ is hit, the diluant consumption will be minimized but at infinitely large final time. Therefore, practical considerations indicate that a constraint $c_1 \leq c_{\mathrm{lim}} - \varepsilon$ should be added to the problem formulation where a small positive ε would balance practical duration of the membrane filtration and diluant consumption.

Optimal diafiltration is then achieved by $\alpha^* = \{0, 1, \infty\}$. Thus the optimal control structure is same as one illustrated in Fig. 6.2 except of middle stage that is done by CVD operation at $c_1 = c_{\mathrm{lim}} - \varepsilon$.

6.2 Optimization at Limiting Flux with Viscosity Dependent Mass Transfer Coefficient

We consider again flux given by (4.1) with $R_1 = 1$ and $R_2 = 0$. A thorough discussion on the model parameters and their concentration-dependency can be found in Zydney (1997). Let us now consider an application where the filtration performance can be described by a

special case of Eq. (4.1) such that

$$q(c_1, c_{\lim}) = k(c_1, c_{\lim}) \ln \frac{c_{\lim}}{c_1}, \tag{6.7}$$

where the limiting (wall) concentration $c_{\lim}$ is assumed to be constant and the mass transfer coefficient k is a function of c_1 and $c_{\lim}$. Note that Eq. (6.7) can be also seen as a slightly generalized form of Eq. (4.1). We consider both laminar and turbulent flow where

$$k = \begin{cases} k_0 e^{\gamma z (c_1 - c_{\lim})} & \text{laminar flow} \\ k_0 e^{\gamma [z(c_1 - c_{\lim}) - c_1/2]} & \text{turbulent flow} \end{cases} \tag{6.8}$$

The constant γ quantifies the concentration dependence of the solution viscosity and z is the exponent in the wall correction factor. More details on these parameters can be found in Aimar and Field (1992).

The optimal switching curve $S(c_1)$ for minimum time control is defined from

$$q + c_1 \frac{\mathrm{d}q}{\mathrm{d}c_1} = 0, \tag{6.9}$$

$$\ln \frac{c_{\lim}}{c_1} \left(1 + \frac{c_1}{k} \frac{\mathrm{d}k}{\mathrm{d}c_1} \right) = 1. \tag{6.10}$$

Note that it again depends on c_1 only and is a constant.

The appropriate optimal concentration for both types of flow is given from nonlinear equation

$$S_{\mathrm{lam}}(c_1) : (c_1 \gamma z + 1) \ln \frac{c_{\lim}}{c_1} = 1, \tag{6.11a}$$

$$S_{\mathrm{tur}}(c_1) : [c_1 \gamma (z - 0.5) + 1] \ln \frac{c_{\lim}}{c_1} = 1. \tag{6.11b}$$

These equations predict that the optimum concentration will be shifted to higher concentrations (i.e. higher than $c_{\lim}/\mathrm{e}$) under laminar flow conditions and lower concentrations under turbulent conditions. Both expressions reduce to the classic result when $\gamma = 0$, i.e. when viscosity effects are negligible.

The minimum diluant operation will be again achieved by concentration step followed by pure dilution. i.e. bang-bang control.

6.3 Optimization at Fixed Pressure with the Osmotic Pressure Model

This model represents a further step in generalization of the use of theoretical models presented in 4.2. To show an applicability of the proposed approach we assume the same problem as above where the limiting concentration c_{lim} is for given c_1 defined by an implicit relation

$$E(c, c_{\text{lim}}) = k \ln \frac{c_{\text{lim}}}{c_1} - \frac{\Delta P - \pi(c_{\text{lim}})}{\mu R_m} = 0. \tag{6.12}$$

In this model, the flux as predicted by concentration polarization theory is equated to the flux as predicted by osmotic pressure theory (4.2) and (Howell et al., 1996). Function $\pi(c_{\text{lim}})$ is defined experimentally, usually as a third degree polynomial with coefficients π_1, π_2, π_3

$$\pi(c_{\text{lim}}) = \pi_1 c_{\text{lim}} + \pi_2 c_{\text{lim}}^2 + \pi_3 c_{\text{lim}}^3. \tag{6.13}$$

For simplicity, only laminar case will be considered, tubular regime can be derived in the same manner. Therefore, the mass transfer coefficient can be written as

$$k = k_0 e^{\gamma z (c_1 - c_{\text{lim}})}, \tag{6.14}$$

where k_0 is mass transfer coefficient without the wall correction factor.

If minimum time operation is considered, the optimal switching curve $S(c_1)$ will be again a constant defined by

$$q + c_1 \frac{\mathrm{d}q}{\mathrm{d}c_1} = 0. \tag{6.15}$$

To derive the expression for derivative of q with respect to c_1, let us note that (6.12) defines an implicit relation between c_1 and c_{lim} and the following holds

$$\frac{\partial c_{\text{lim}}}{\partial c_1} = -\frac{\frac{\partial E}{\partial c_1}}{\frac{\partial E}{\partial c_{\text{lim}}}}, \tag{6.16a}$$

$$\frac{\partial E}{\partial c_1} = \frac{\partial k}{\partial c_1} \ln \frac{c_{\text{lim}}}{c_1} - k \frac{1}{c_1}, \tag{6.16b}$$

$$\frac{\partial E}{\partial c_{\text{lim}}} = \frac{\partial k}{\partial c_{\text{lim}}} \ln \frac{c_{\text{lim}}}{c_1} + k \frac{1}{c_{\text{lim}}} + \frac{1}{\mu R_m} \frac{\partial \pi(c_{\text{lim}})}{\partial c_{\text{lim}}}. \tag{6.16c}$$

Then, the following holds

$$\frac{\mathrm{d}q}{\mathrm{d}c_1} = \frac{\partial q}{\partial c_1} + \frac{\partial q}{\partial c_{\text{lim}}} \frac{\partial c_{\text{lim}}}{\partial c_1}, \tag{6.17a}$$

$$\frac{\mathrm{d}q}{\mathrm{d}c_1} = \frac{\partial k}{\partial c_1} \ln \frac{c_{\text{lim}}}{c_1} - \frac{k}{c_1} + \left(\frac{\partial k}{\partial c_{\text{lim}}} \ln \frac{c_{\text{lim}}}{c_1} + \frac{k}{c_{\text{lim}}} \right) \frac{\partial c_{\text{lim}}}{\partial c_1}. \tag{6.17b}$$

The optimal switching curve $S(c_1)$ can be derived as

$$0 = \left(\frac{1}{c_{\text{lim}}} - \gamma z \ln \frac{c_{\text{lim}}}{c_1}\right) \ln \frac{c_{\text{lim}}}{c_1} + \frac{1}{k} \frac{1}{\mu R_m} \frac{\partial \pi(c_{\text{lim}})}{\partial c_{\text{lim}}} \left(\ln \frac{c_{\text{lim}}}{c_1}(1 + \gamma z c_1) - 1\right). \tag{6.18}$$

The optimal concentration c_1 and the corresponding wall concentration c_{lim} can then be calculated from the system of nonlinear equations (6.12) and (6.18).

Both rejection coefficients are constant again and therefore minimum diluant operation is defined with α^* being on constraints (concentration and consequent dilution).

6.4 Case Study 1: Separation of Lactose from Proteins

We consider a process described in Rajagopalan and Cheryan (1991) where lactose is separated from milk proteins by UF combine with diafiltration. Both retention coefficients are constant $R_1 = 1$, $R_2 = 0$. We will assume $\alpha \geq 0$. Permeate flow was determined experimentally as

$$q(c_1, c_2) = b_0 + b_1 \ln c_1 + b_2 \ln c_2 = 63.42 - 12.439 \ln c_1 - 7.836 \ln c_2, \tag{6.19}$$

where c_1 is concentration of proteins and c_2 denotes concentration of lactose.

The optimum concentration curve for the minimum time problem depends on both concentrations and is given by (5.12) as

$$\begin{aligned} S(c_1, c_2) &= q + c_1 \frac{\partial q}{\partial c_1} + c_2 \frac{\partial q}{\partial c_2}, \\ 0 &= b_0 + b_1 + b_2 + b_1 \ln c_1 + b_2 \ln c_2. \end{aligned} \tag{6.20}$$

Once these optimal concentrations are obtained the control is calculated from (5.27)

$$\alpha_{\text{sing}}(t) = \frac{\frac{\partial S}{\partial c_1} c_1}{\frac{\partial S}{\partial c_1} c_1 + \frac{\partial S}{\partial c_2} c_2} = \frac{b_1}{b_1 + b_2}. \tag{6.21}$$

As we can see, even if the optimal concentration curve depends on both concentrations, the corresponding optimal control is constant and less than one due to special expression for q.

We consider to drive concentrations from initial point $[c_{1,0}, c_{2,0}] = [3.3, 5.5]$ to final point $[c_{1,\text{f}}, c_{2,\text{f}}] = [9.04, 0.64]$. To perform this task in minimum time we use a three step strategy (see state diagram in Fig. 6.3):

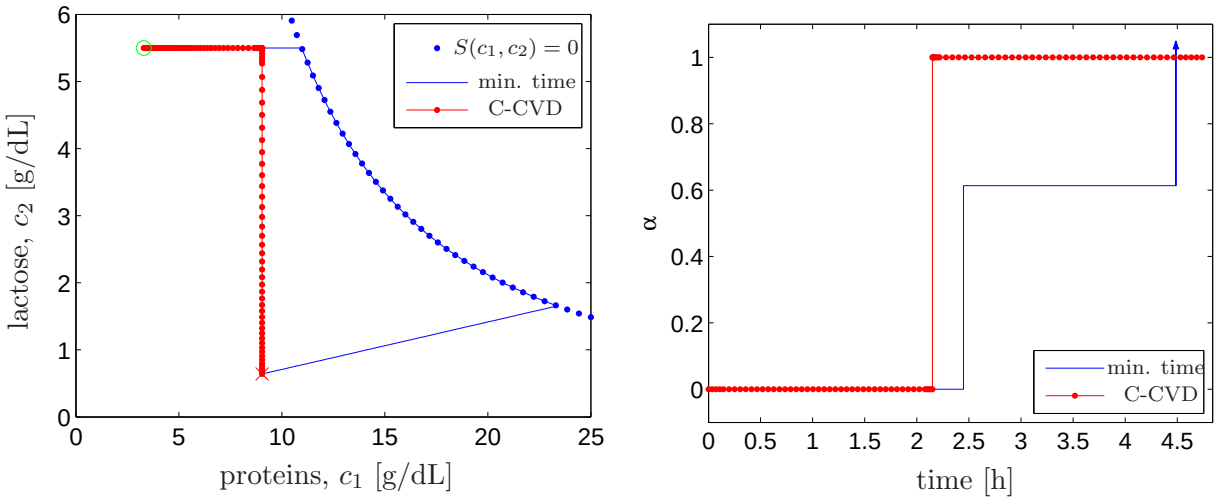


Figure 6.3: Separation of lactose from proteins: comparison of minimum time and C-CVD control strategy in concentration diagram (left plot) and corresponding control (right plot).

1. Start at green circle, horizontal line: pure ultrafiltration until we arrive at optimal surface $S(c_1, c_2) = 0$.

2. Stay on this surface using constant control $\alpha = b_1/(b_1 + b_2) = 0.61$ until the concentration ratio is the same as the final one: $c_1(t)/c_2(t) = c_{1,\mathrm{f}}/c_{2,\mathrm{f}}$.

3. Follow the line towards origin: use pure dilution step to arrive at the final point (red cross).

The resulting final time in this case is 4.49 hours. This can be compared to the operation described in Rajagopalan and Cheryan (1991) where two step process C-CVD (UF-CVD) was used. This traditional operation takes for the same initial and final conditions 4.74 hours, an increase of 5.6%. As we can see from the right diagram in Fig. 6.3, traditional CVD step ($\alpha = 1$) starts earlier but it takes more time to reach the final point as the VVD step ($\alpha = 0.61$) in minimum time control. There, it is assumed that the last step (upward arrow) takes no time. Although this is not true in reality, we can simply move the dilution step out the batch to further processing.

The overall minimum time strategy is sketched in Fig. 6.4 where horizontal solid lines represent evolution of concentrations during the concentration (UF) step and dashed lines during pure dilution ($\alpha = \infty$). Arrows in these lines denote directions, in which the

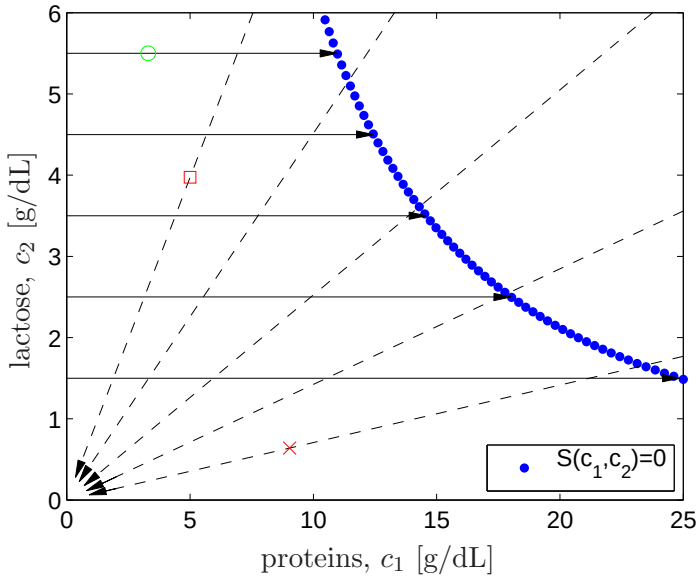


Figure 6.4: Separation of lactose from proteins: analytical minimum time control in concentration diagram.

respective operations influence concentrations. Previously used initial and final points are depicted again to illustrate how the minimum time optimal strategy is chosen. We note that it seems theoretically possible to use two step strategy starting with dilution step followed by ultrafiltration. However, the resulting final time will be much longer. As a practical rule of thumb it is necessary to consider only such strategies that approach the optimal concentration curve. Also note that it is not possible to use dilution and ultrafiltration steps more times. Optimal control theory does not allow this arbitrary switching and the resulting trajectory can consists at most of three steps.

Consider now a case where we want to arrive at final point $[5, 3.97]$ (red square in Fig. 6.4) starting from the same initial point. As shown in Fig. 6.4, it is not admissible to use three step operation since once we would reach the surface $S(c_1, c_2)$ (by using UF) it would not be possible anymore to reach the final point neither by using UF nor pure dilution. Thus, the middle step is skipped in this case and minimum time operation is attained only by using ultrafitration and pure dilution operation. Order of these operations is again not arbitrary and it is such that the resulting curve in state diagram is as close as possible to optimal surface $S(c_1, c_2)$. The switching moment between the steps is determined by the concentration ratio equal to $c_{1,\mathrm{f}}/c_{2,\mathrm{f}}$.

The optimal concentration surface does not exist for the minimum diluant problem and

Table 6.1: Permeate volumetric flowrate relation constants (Data taken from Jaffrin and Charrier (1994)).

Constant	Value
b1	2.877
b2	1.698E-01
b3	1.874E-02
b4	5.708E-04
b5	-2.394E-04
b6	9.334E-05

the resulting optimal operation is of bang-bang type. To illustrate this we could construct a diagram similar to Fig. 6.4 by prolonging the horizontal lines corresponding to pure ultrafiltration.

6.5 Case Study 2: Albumin – Ethanol Separation

This ultrafiltration/diafiltration process was originally studied in Jaffrin and Charrier (1994). The flow q was determined experimentally as

$$q(c_1, c_2) = \frac{1}{b_1 + b_2 c_1 + b_3 c_2 + b_4 c_1 c_2 + b_5 c_1^2 + b_6 c_2^2}, \tag{6.22}$$

where b_i are constants, as reported by Jaffrin and Charrier (1994), can be found in Table 6.1.

Both retention coefficients are constant $R_1 = 1$, $R_2 = 0$ and $\alpha \in [0, 1]$. Normalized process time is being used, that enables straightforward scale-up calculations. Normalized process time is defined as the time necessary to process an initial feed solution of $0.0666\,\mathrm{m}^3$ which corresponds to $1\,\mathrm{kg}$ of albumin (initial albumin concentration is $15\,\mathrm{kg\,m}^{-3}$) being separated with $1\,\mathrm{m}^2$ membrane. We investigate different cases of initial concentration of ethanol ($c_{2,0}$) and of restriction for final concentration of albumin ($c_{1,f}$). These are summarized in Table 6.2.

Finding optimal control numerically. In order to find optimal operation this diafiltration process numerically we may use numerical techniques presented in Section 3.3.

Table 6.2: Initial and final conditions on macro-/micro-solute concentrations.

Case	$c_{1,0}$ $[\mathrm{kg\,m^{-3}}]$	$c_{1,f}$ $[\mathrm{kg\,m^{-3}}]$	$c_{2,0}$ $[\mathrm{kg\,m^{-3}}]$	$c_{2,f}$ $[\mathrm{kg\,m^{-3}}]$
1	15	80	98.35	0.1
2	15	80	146.3	0.1
3	15	80	194.3	0.1
4	15	120	98.35	0.1
5	15	120	146.3	0.1
6	15	120	194.3	0.1
7	15	240	98.35	0.1
8	15	240	146.3	0.1
9	15	240	194.3	0.1

Here we use CVP method with gradients to optimized variables (unknown parameters of discretized trajectory $\alpha(t)$) computed by sensitivity equations method.

Function $\alpha(t)$ can be approximated as piece-wise constant (PWC) or piece-wise linear. Approximation with a low value of PWC segments (say 2–3) can produce results that are compatible with known diafiltration strategies as C-CVD and VVD. As number of PWC segments becomes larger, we can decide whether traditional strategies are sufficient or if there is some room for improvement using more advanced $\alpha(t)$ trajectories.

For the case of approximation of $\alpha(t)$ by one constant and one linear segment, the same optimum has been observed for both optimization problems. The improvement using linear compared to constant $\alpha(t)$ is in average 9.7% for the minimum time operation and 42.3% for the minimum diluant problem.

We have chosen 2, 3, and 40 PWC segments in order to investigate the impact of choosing PWC control strategy to minimize the total time of process operation. Table 6.3 summarizes results obtained by several PWC functions $\alpha(t)$ for minimum time problem. Starred cost function $\mathcal{J}_1^*$ represents the minimum time attained, whereas the unstarred cost function $\mathcal{J}_2$ means evaluation of the corresponding total diluant consumption.

Compared to constant or linear case, advantages of using PWC profiles are evident.

Table 6.3: Minimum operation times and diluant consumptions for different $N\times$ PWC $\alpha(t)$.

Case	2×PWC $\alpha(t)$		3×PWC $\alpha(t)$		40×PWC $\alpha(t)$	
	$\mathcal{J}_1^*$[h]	$\mathcal{J}_2$[m^3]	$\mathcal{J}_1^*$[h]	$\mathcal{J}_2$[m^3]	$\mathcal{J}_1^*$[h]	$\mathcal{J}_2$[m^3]
1	2.04	0.086	2.04	0.086	2.04	0.088
2	2.30	0.104	2.30	0.104	2.29	0.103
3	2.54	0.118	2.54	0.123	2.54	0.124
4	1.98	0.058	1.98	0.058	1.98	0.059
5	2.24	0.075	2.24	0.075	2.24	0.076
6	2.49	0.088	2.48	0.095	2.48	0.096
7	1.84	0.030	1.84	0.030	1.84	0.030
8	2.11	0.044	2.11	0.044	2.11	0.047
9	2.36	0.055	2.35	0.067	2.35	0.063

The average gain is 64.8% for diluant problem and 14.3% for minimum time problem in comparison with constant α.

If treating $\alpha(t)$ as a PWC function, obtained results show that there is a similarity in trajectories of optimal $\alpha(t)$ for Cases 1,4,7; Cases 2,5,8; and for Cases 3,6,9. When Cases 1,4,7 are considered, two and three PWC segments produce the same optimal operation characterized as C-CVD process with $\alpha(t) = \{0, 1\}$ with appropriate time lengths.

For other cases, two and three PWC segments produce similar solutions that are a combination of VVD and C-CVD processes with $\alpha(t) = \{\alpha^1, 1\}$ where $\alpha^1 > 0$.

Although a finer PWC approximation (forty PWC segments) exhibits a different optimal $\alpha(t)$ trajectory, minimum operation time stays almost unchanged and differences in final time between 3 and 40 segments are negligible. Hence, minimum is in this case flat, i.e. final time value is not strongly influenced by shifting $\alpha(t)$ trajectory from the optimal to traditional diafiltration operation (C-CVD).

We have again chosen 2, 3, and 40 PWC segments in order to investigate the impact of choosing PWC control strategy to minimize the diluant consumption. Table 6.4 summarizes the results.

Starred cost function $\mathcal{J}_2^*$ represents the minimum diluant consumption attained, whereas the unstarred cost function $\mathcal{J}_1$ means the corresponding total time.

Table 6.4: Operation times and minimum diluant consumptions for different $N\times$ PWC $\alpha(t)$.

Case	2×PWC $\alpha(t)$		3×PWC $\alpha(t)$		40×PWC $\alpha(t)$	
	$\mathcal{J}_1$[h]	$\mathcal{J}_2^*$[m^3]	$\mathcal{J}_1$[h]	$\mathcal{J}_2^*$[m^3]	$\mathcal{J}_1$[h]	$\mathcal{J}_2^*$[m^3]
1	2.04	0.086	2.04	0.086	2.04	0.086
2	2.31	0.091	2.31	0.091	2.31	0.091
3	2.59	0.095	2.59	0.095	2.55	0.095
4	1.98	0.057	1.98	0.057	1.98	0.057
5	2.26	0.061	2.26	0.061	2.24	0.061
6	2.55	0.063	2.55	0.063	2.52	0.063
7	1.84	0.029	1.84	0.029	1.85	0.029
8	2.13	0.030	2.13	0.030	2.13	0.030
9	2.42	0.032	2.42	0.032	2.42	0.032

The average gain in the minimum diluant consumption is 69% comparing to constant $\alpha(t)$ case. C-CVD (bang-bang control) process operation was proved to be optimal in all cases and only 2 PWC segments are needed. For different number of PWC segments, obtained minimum final times differ only slightly from those computed in previous case. The minimum diluant consumption and minimum time operation is the same for Cases 1,4,7. If concentration $c_{2,0}$ is increased, it is possible to obtain optimal operation with substantially less diluant as in the minimum time problem but at the expense of longer processing times.

Finding optimal control analytically. Here we will compare our findings obtained by numerical procedure with analytically constructed optimal control. We consider only Cases 1, 2, and 3. Our intention is to show that fine PWC approximation of optimal control trajectory provides satisfactory results and thus is suitable to use also for cases when analytical solution is not available.

The optimum concentration curve for the minimum time problem depends on both

concentrations and is given by (5.12) as

$$S(c_1, c_2) = q + c_1 \frac{\partial q}{\partial c_1} + c_2 \frac{\partial q}{\partial c_2},$$
$$0 = b_1 - b_5 c_1^2 - c_1 c_2 b_4 - b_6 c_2^2. \tag{6.23}$$

Once these optimal concentrations are obtained the control is calculated from (5.27)

$$\alpha_{\text{sing}}(t) = \frac{\frac{\partial S}{\partial c_1} c_1}{\frac{\partial S}{\partial c_1} c_1 + \frac{\partial S}{\partial c_2} c_2} = \frac{0.5 b_4 c_1 c_2 + b_5 c_1^2}{b_5 c_1^2 + b_4 c_1 c_2 + b_6 c_2^2}. \tag{6.24}$$

Figures 6.5, 6.6 and 6.7 show and compare the time-optimal control of diafiltration process for chosen cases found numerically and analytically. Even if analytical and numerical curves seem to be different at singular arcs, the resulting final times are practically the same.

Both initial and final concentrations in Case 1 are below the optimal concentration curve. Therefore, the corresponding optimal operation is to perform UF first until the optimal curve is attained. In the second step, α is given by (6.24) until the final concentration of albumin $c_{1,\text{f}} = 80\,\text{kg}\,\text{m}^{-3}$ is reached. The final step is CVD until the final concentration of ethanol is reached.

Cases 2 and 3 differ from the Case 1 as they start above the optimal concentration curve. Therefore, the first step is CVD (upper constraint on α is 1). Its duration depends on the distance of the initial point from the optimal curve. The second and the third steps are then the same as before.

We can observe that C-CVD strategy is nearly time-optimal even if the minimum time control is quite different from that used in C-CVD. This results from the restriction on upper value of control α. If this value is raised such that pure dilution step is allowed the resulting operation times will dramatically drop down.

In the case of minimum diluant problem bang-bang type of control (C-CVD operation) was observed numerically. Results derived here confirm this behavior as both retention coefficients are constant. Comparison with VVD strategy shows 61% optimality loss in all considered cases.

6.6 Case Study 3: Dye – Salt Separation

We consider the nanofiltration (NF) model reported in Lau and Ismail (2010). In their study, response surface methodology (RSM) was employed to evaluate the separation per-

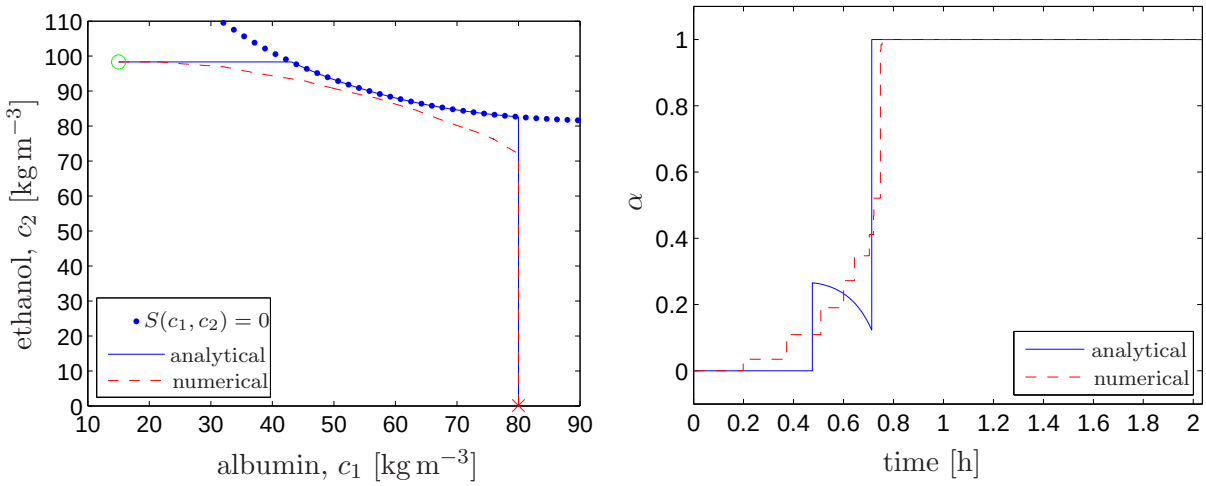


Figure 6.5: Analytical and numerical minimum time control for Case 1. Left plot – optimal concentrations diagram, right plot – optimal $\alpha(t)$.

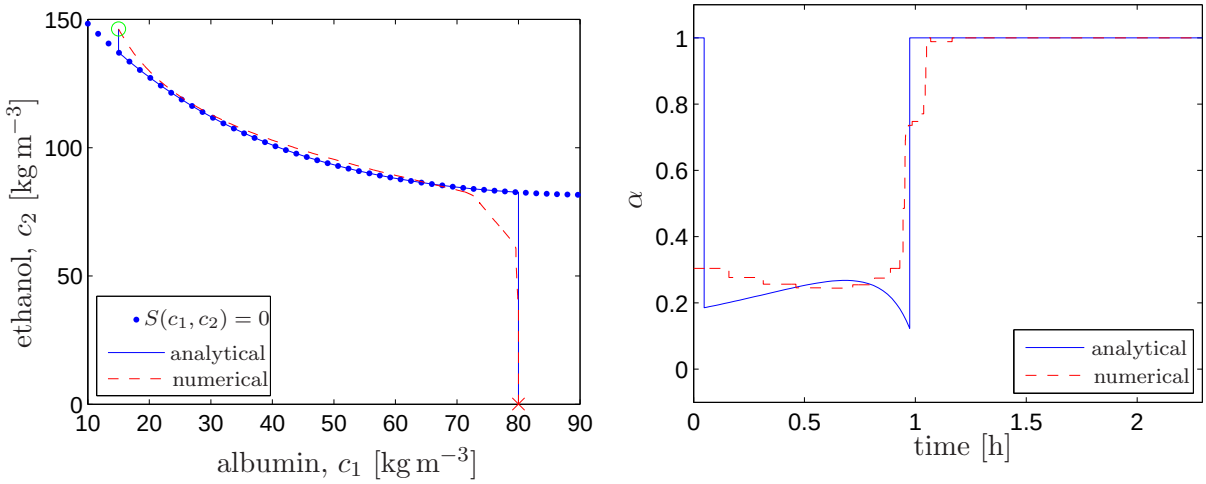


Figure 6.6: Analytical and numerical minimum time control for Case 2. Left plot – optimal concentrations diagram, right plot – optimal $\alpha(t)$.

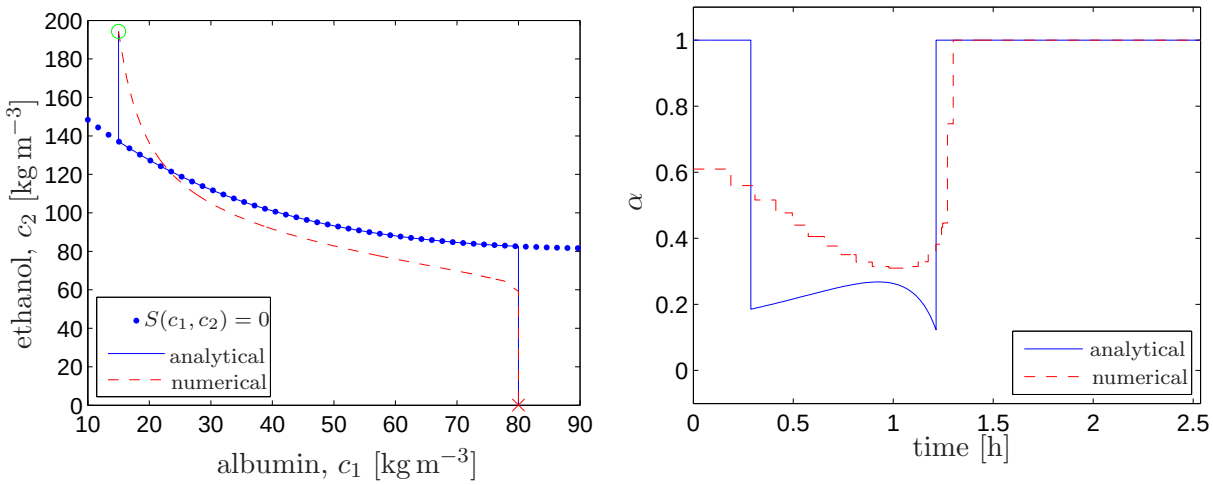


Figure 6.7: Analytical and numerical minimum time control for Case 3. Left plot – optimal concentrations diagram, right plot – optimal $\alpha(t)$.

Table 6.5: Design factors and their levels (adopted from Lau and Ismail (2010)).

Factor	Code	Unit	Factor levels	
			Low(−)	High(+)
Pressure	A	bar	4	8
Temperature	B	°C	28	50
pH	C	-	4	11
Dye concentration	D	ppm	100	400
Salt concentration	E	ppm	1000	6000

formance of an NF membrane in the removal of salt and reactive dye by varying different variables such as pressure, temperature, pH, dye concentration and salt concentration. According to half fractional design of experiments (DoE), twenty-nine experiments were carried to investigate the effect of five inputs (i.e. pressure, temperature, pH, dye concentration, and salt concentration) on three responses (i.e. permeate flux, dye rejection, and salt rejection). The design factors and their levels are shown in Table 6.5. The permeation of salt was found to be greatly influenced by pressure, pH and salt concentration whereas the rejection of dye remained constant regardless of the changes in the variables. The mean value of the salt rejection for the entire experimental data set is 98.0%. The resulting surface responses for the salt rejection and the permeate flux in terms of coded factors are

Table 6.6: Model parameters.

constant	value
b_1	0.9800
b_2	0.7647
b_3	1.8080×10^{-5}
b_4	5.8607×10^{-7}
b_5	2.5066×10^{-10}
b_6	4.0600×10^{-11}

given as

$$Y_1 = 83.26 + 2.79A + 8.37C - 4.52E - 1.96AC, \tag{6.25a}$$

$$Y_3 = 6.31 \cdot 10^{-7} + 1.89 \cdot 10^{-7}A - 1.67 \cdot 10^{-8}D - 1.30 \cdot 10^{-7}E - \\ - 6.07 \cdot 10^{-8}C^2 - 2.85 \cdot 10^{-8}AE - 2.096.31 \cdot 10^{-8}BD, \tag{6.25b}$$

where Y_1 is the salt rejection expressed in percentage and Y_3 is the permeate flux given in $\mathrm{m\,s^{-1}}$.

In this case study, we consider a textile waste stream with the initial dye and salt concentrations, $c_{1,0} = 100\,\mathrm{ppm}$ and $c_{2,0} = 4000\,\mathrm{ppm}$, that is to be processed to meet the quality constraints of the final product, $c_{1.\mathrm{f}} = 400\,\mathrm{ppm}$ and $c_{2,\mathrm{f}} = 1000\,\mathrm{ppm}$. Lau and Ismail (2010) have found that the salt rejection increases with pressure and decreases with feed pH. Thus, we fix the pressure at 4 bar, the pH at 4, and additionally, the temperature at 50°C. Using original scale instead of the coded factors and taking into account the above mentioned process conditions, the membrane response can be formulated as follows

$$R_1 = b_1, \tag{6.26a}$$

$$R_2(c_2) = b_2 - b_3c_2, \tag{6.26b}$$

$$q(c_1, c_2) = b_4 - b_5c_1 - b_6c_2, \tag{6.26c}$$

where b_i are constants that are listed in Table 6.6.

The dye rejection R_1 is independent of the feed composition and we can assume that it is sufficiently close to unity. In this case, because $R_{11} = R_{12} = 0$ and $R_1 \approx 1$, the minimum time state curve is reduced to

$$S_{\mathrm{time}}(c_1, c_2) = (R_2 - 1)(q + c_1q_1 + c_2q_2) + q(c_1R_{21} + c_2R_{22}) = 0. \tag{6.27}$$

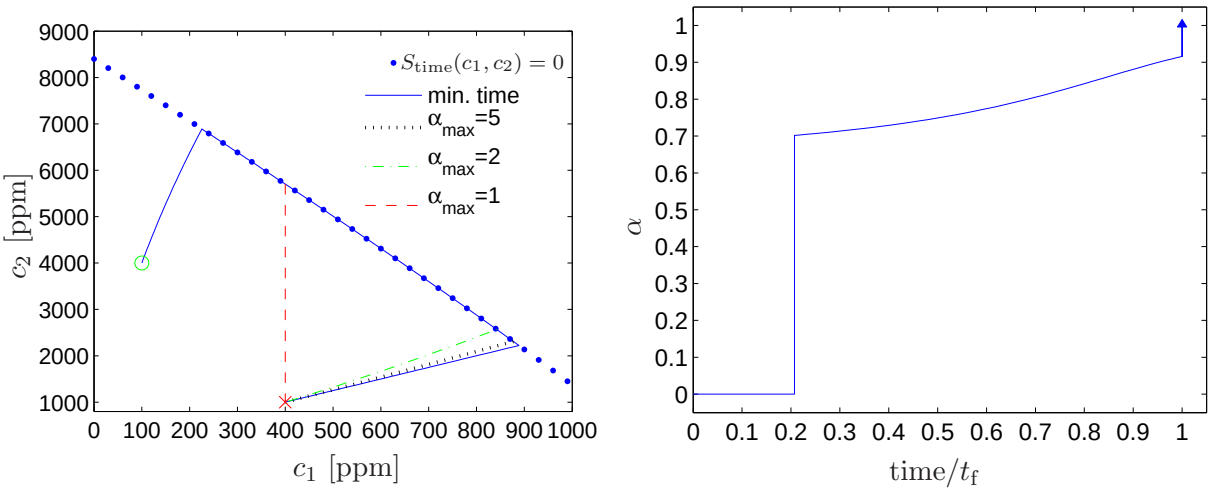


Figure 6.8: Dye – salt separation: optimal operation. Left plot – optimal concentrations diagram with different values of $\alpha_{\max}$, right plot – optimal $\alpha(t)$.

Using the membrane response formulas given in (6.26b) and (6.26c) we then obtain

$$S_{\text{time}}(c_1, c_2) = (b_3 c_2 - b_2 + 1)\,(2b_5 c_1 - b_4 + 2b_6 c_2) + b_3 c_2\,(b_5 c_1 - b_4 + b_6 c_2) = 0. \tag{6.28}$$

The singular control $\alpha(t)$ is calculated as

$$\alpha(t) = \frac{\frac{\partial S}{\partial c_1} c_1}{\frac{\partial S}{\partial c_1} c_1 + \frac{\partial S}{\partial c_2} c_2}, \tag{6.29}$$

resulting in

$$\begin{aligned}\alpha(t) = {} & \frac{c_2\,(2b_2 b_6 - 2b_2^2 b_6 - 2b_2 b_3 b_4) + c_2^2\,(2b_3^2 b_4 - 2b_3 b_6 + 8b_2 b_3 b_6) - 6b_3^2 b_6 c_2^3}{2(b_5 c_1 + b_6 c_2 - b_2 b_5 c_1 - b_3 b_4 c_2 - b_2 b_6 c_2 + 3b_3 b_6 c_2^2 + 3b_3 b_5 c_1 c_2)} \\ & + \frac{c_1\,(2b_1 b_5 - 2b_1 b_2 b_5) + c_1 c_2\,(3b_1 b_3 b_5 + 3b_2 b_3 b_5) - 3b_3^2 b_5 c_1 c_2^2}{2(b_5 c_1 + b_6 c_2 - b_2 b_5 c_1 - b_3 b_4 c_2 - b_2 b_6 c_2 + 3b_3 b_6 c_2^2 + 3b_3 b_5 c_1 c_2)}.\end{aligned} \tag{6.30}$$

The optimal control is shown in Fig. 6.8. Both initial and final concentrations are located under the optimal concentration curve and the optimal process is a three-step process. The first step is concentration mode ($\alpha = 0$) until optimum concentration curve presented by (6.27) is reached. The second step is a dynamic-volume diafiltration with non-constant $\alpha(t)$ where the diluant usage is given by (6.30). This step finishes when the concentration ratio is the same as the final one: $c_1(t)/c_2(t) = 0.4$. Finally, the third step is a pure dilution mode with $\alpha = \infty$.

Figure 6.8 shows for comparison the concentration profiles for different choice of maximum value of α. As noted above, the limiting cast $\alpha = \infty$ can simply be realized by

Table 6.7: Comparison of time optimality loss (Δ) between optimal control, optimal control with different $\alpha_{\max}$ and traditionally used strategies.

control strategy	C-DVD ($\alpha_{\max}$=5)	C-DVD ($\alpha_{\max}$=2)	C-DVD ($\alpha_{\max}$=1)	C-CVD	VVD
Δ	0.1%	0.6%	8.3%	14.0%	55.3%

postponing the pure dilution step after the end of batch processing once the final solution is prepared for the next operation. Another possibility would be to constrain $\alpha_{\max} \approx 5$ where the difference to optimal operation is not large.

Table 6.7 shows comparison of time optimality loss between optimal control ($\alpha_{\max} = \infty$), optimal control with $\alpha_{\max}$ restricted to different values and traditional control approaches. Here we can see that the difference between optimal control and optimal control with $\alpha_{\max} = 5$ is practically negligible. This difference increases, but not dramatically, if α is constrained from above by 2. However, it becomes significant (8.3% of optimality loss) in the case of $\alpha_{\max} = 1$. Comparison with traditional control strategies shows 14% slower process with C-CVD approach. Finally, the VVD approach controls the process slower by more than 50%.

Also note that traditional operation is constrained with $c_1 < 400\,\text{ppm}$ whereas the proposed optimal operation needs this constraint approximately twice as large. It may happen that $S(c_1, c_2)$ is located outside of the experimentally investigated region of c_1 and c_2 where the membrane response model is not validated. It seems that the common practice is that investigators focus on obtaining experimental data from the design space bounded by ($c_{1,0}$, $c_{2,0}$) and ($c_{1,\text{f}}$, $c_{2,\text{f}}$) coordinates whereas optimal operation might be performed outside of this area. In other words, optimal operation might involve over-concentration or dilution of the solution and thus, a bigger design space should be considered during the experimentation phase.

Recalling that $R_1 = 1$ is assumed, the optimal state curve for the minimum diluant problem is defined as

$$S_{\text{diluant}}(c_1, c_2) = R_2 - 1 + c_1 \frac{\partial R_2}{\partial c_1} + c_2 \frac{\partial R_2}{\partial c_2} = 0. \tag{6.31}$$

Using the membrane response formulas given in (6.26b) and (6.26c), the optimal state curve can be written as

$$S_{\text{diluant}}(c_2) = b_2 - 2b_3 c_2 - 1 = 0. \tag{6.32}$$

This results in a single equation involving only variable c_2. Solving this equation yields a negative value ($c_2 = -6508$) that is technically not feasible. The optimal control is then of bang-bang type: a two-step process where the first step is a concentration step with $\alpha = 0$ and the second is a dilution mode operation applying the maximum value of α.

6.7 Case Study 4: Sucrose – Sodium Chloride Separation

This case study is taken from Fikar et al. (2010) where numerical methods of dynamic optimization (orthogonal collocation) were used to derive the optimal control of nanofiltration/diafiltration process using an economic cost function.

This case study represents diafiltration system with one variable retention coefficient (R_1 is almost constant and equal to one) and the empirical relations for q and R_2 as functions of feed composition are as follows:

$$q = U_1(c_2)\mathrm{e}^{U_2(c_2)c_1}, \tag{6.33a}$$

$$R_2 = V_1(c_2)\mathrm{e}^{V_2(c_2)c_1}, \tag{6.33b}$$

where S_1, S_2, W_1, W_2 are second degree polynomials in c_2

$$U_1(c_2) = u_1c_2^2 + u_2c_2 + u_3, \tag{6.34a}$$

$$U_2(c_2) = u_4c_2^2 + u_5c_2 + u_6, \tag{6.34b}$$

$$V_1(c_2) = v_1c_2^2 + v_2c_2 + v_3, \tag{6.34c}$$

$$V_2(c_2) = v_4c_2^2 + v_5c_2 + v_6, \tag{6.34d}$$

and u_{1-6} and v_{1-6} are coefficients that were determined from laboratory experiments with the process solution (Kovács et al., 2009). It is assumed that $\alpha \in [0, 1]$.

It is desired to concentrate sucrose and dilute sodium chloride in solution from their initial concentrations given by point $[c_{1,0}, c_{2,0}] = [10, 250]$ to final concentrations represented by the point $[c_{1,\mathrm{f}}, c_{2,\mathrm{f}}] = [50, 50]$.

The optimum concentration curve for the minimum time problem depends on both concentrations and is given by (5.12) as

$$S_{\mathrm{time}}(c_1, c_2) = (R_2 - 1)\left(q + c_1\frac{\partial q}{\partial c_1} + c_2\frac{\partial q}{\partial c_2}\right) + q\left(c_1\frac{\partial R_2}{\partial c_1} + c_2\frac{\partial R_2}{\partial c_2}\right) = 0. \tag{6.35}$$

The optimum concentration curve corresponding to the minimum diluant problem is given analogically as

$$S_{\text{diluant}}(c_1, c_2) = R_2 - 1 + c_1 \frac{\partial R_2}{\partial c_1} + c_2 \frac{\partial R_2}{\partial c_2} = 0. \tag{6.36}$$

Both curves have been found using numerical nonlinear equation solvers. Figure 6.9 shows the optimal control of diafiltration process for considered case. Results show that even if the optimal concentration curve expressions look entirely different, solutions to both optimal control problems are nearly the same: minimum-time approach takes 10.24 hours and 0.143 m^3 of diluant and minimum-diluant approach takes 10.25 hours and consumes 0.143 m^3 of diluant. In contrast to that, a traditional treatment with NF followed by CVD and ended by another NF (C-CVD-C) step lasts 14.46 hours and uses 0.256 m^3 of diluant. Here 5 and 0.72 are pre-concentration and post-concentration factors, respectively.

Although the two-step approach ($\alpha = \{0, 1\}$) would result in faster process, it would yield high concentrations of salt during the process run that lay out of the range studied in Kovács et al. (2009). The model is not validated through experiments for this regime, thus, we have to exclude this strategy from further discussion. In general, a great care is needed when using empirical models, especially polynomials, for predicting flux and rejections out of the validated range. In such cases, application of mechanism-driven models could be considered instead. Note that even complex physical models can be easily treated by the here proposed optimization methodology. Physical models can be used first to compute membrane response for a defined set of c_1 and c_2 that covers the entire area of question, and then simplified by fitting some simpler empirical relations.

VVD approach is clearly sub-optimal since it takes 22.753 hours and 0.505 m^3 of diluant. Another interesting result here is that C-VVD (process duration 14.07 hours, diluant consumption 0.253 m^3, pre-concentration factor 3.69) approach is faster than C-CVD-C. However, this is caused by the previously mentioned inadmissibility of two-step C-CVD operation. Table 6.8 summarizes how much we gain by using of optimal control in comparison with traditional strategies.

Let us consider another particular case taken from Fikar et al. (2010). The amount of sodium chloride was minimized at the end of 6 hours of NF/DF process run with optimal α being of bang-bang type. Using optimal α the concentrations were shifted from initial state of $[c_{1,0}, c_{2,0}] = [150, 300]$ to arrive at final state $[c_{1,\mathrm{f}}, c_{2,\mathrm{f}}] = [440, 23.38]$.

Let us suppose an inverse problem. We aim to find optimal time operation to start and

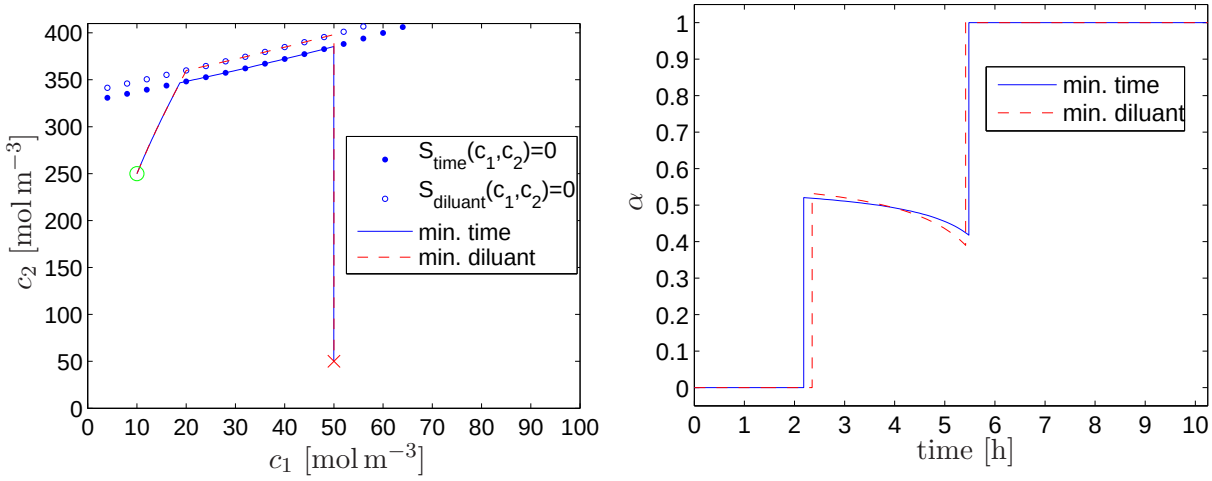


Figure 6.9: Analytical optimal control of sucrose–sodium chloride separation. Upper plot – optimal concentrations diagram, lower plot – optimal $\alpha(t)$.

Table 6.8: Comparison of optimality loss (Δ) between optimal control and traditionally used strategies.

	Δ_{time}	Δ_{diluant}
C-CVD-C	41%	79%
C-VVD	37%	77%
VVD	122%	253%

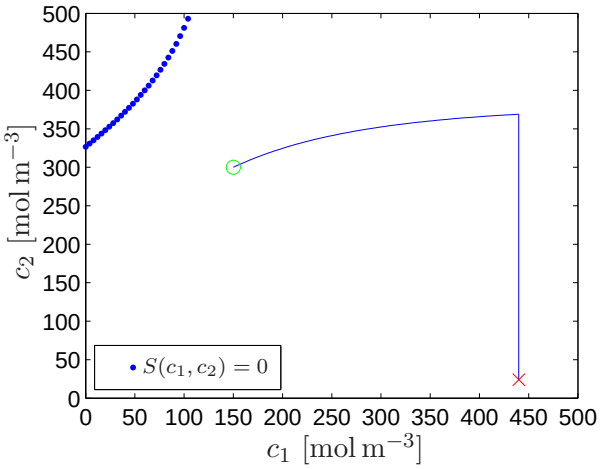


Figure 6.10: Analytical time-optimal control of sucrose–sodium chloride separation. Case A taken from Fikar et al. (2010).

finish UF/DF process with above mentioned initial/final conditions. Since the problem is inverse the optimal solution is the same (bang-bang) as observed for non-inverse one. It is visualized by concentration diagram in Fig. 6.10. First, α equal to zero is taken to arrive at prescribed final concentration of macro-solute. The second step is CVD (α at maximum). The reason of having bang-bang optimal solution can be seen in the fact that the curve $S_{\text{time}}(c_1, c_2) = 0$ cannot be reached by any means (any α) on way from initial to prescribed final point.

6.8 Case Study 5: Radiopaque – Ethylene Glycol Separation

We treat the case study taken from Lutz (1997) where authors studied filtration using reverse osmosis membrane to treat a solution containing 12 g/dL of radiopaque component (c_1) and 0.5 g/dL of ethylene glycol (c_2) to end up with the product with concentrations: 40 g/dL of radiopaque and 0.01 d/dL of ethylene glycol. Experimentally obtained mem-

brane characteristics are as follows

$$q = -29.19 \ln c_1 + 118.1, \tag{6.37a}$$

$$R_1 = 1 - (0.01c_1 + 0.25c_2 + 0.1), \tag{6.37b}$$

$$R_2 = 1 - (0.0073c_1 + 0.813). \tag{6.37c}$$

For the purpose of this study constants which characterize rejection of radiopaque were slightly changed to reflect the situation where rejection R_1 is not close to one.

This example represents a situation when we are not able to obtain expression for optimal concentration surface analytically. We proceed as suggested previously and derive an expression for singular optimal control from (5.16). Then we use numerical optimization to find corresponding lengths of intervals for boundary values of control as well as for singular one. Results indicate that the optimal control trajectory consists of three parts: RO, singular arc, and RO. Numerical procedure determines lengths of all these parts. Once the structure and lengths of respective intervals are fixed, we can operate the process optimally with singular control (5.16) in the middle part.

Fig. 6.11 shows optimal evolution of concentrations under minimum time control α. When compared with traditional control strategies, minimum time strategy saves 9% of process time in comparison with C-CVD (CVD step done at concentration c_{lim}/e) and 18% of process time when compared to VVD control strategy.

In minimum diluant case, although that it is possible that optimal surface exists, it did not appear for given initial and final conditions. The optimal control is of bang-bang type.

6.9 Discussion

This part of the work deals with batch concentration/diafiltration problems that often occur in the RO, NF, UF, and MF engineering practice. We have employed optimal control theory and derived an analytical solution to the problem that involves complete rejection of macro-solute ($R_1 = 1$), concentration-dependent rejection of micro-solute ($R_2 = R_2(c_1, c_2)$), and a general flux model ($q = q(c_1, c_2)$). The extension of this problem to concentration-dependent rejection of macro-solute ($R_1 = R_1(c_1, c_2)$) remains analytically unsolved. However, for this general case we have developed an efficient numerical procedure that exploits the findings of our theoretical analysis and considerably reduces the required computational efforts.

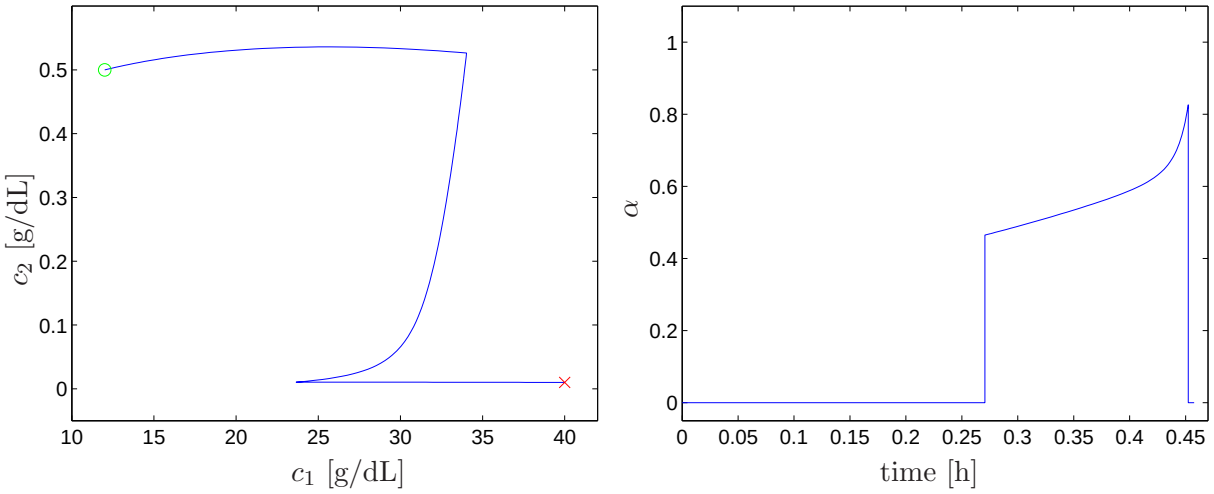


Figure 6.11: Minimum time control of radiopaque - ethylene glycol separation.

We provide a step-by-step procedure to compute the optimal diluant utilization. By applying this procedure, one can determine the optimal time-varying profile of wash-water addition for the entire operation. In some cases, the computed optimal profile is found to be a sequence of conventionally-used steps (i.e. concentration mode, constant-volume diafiltration, variable-volume diafiltration). The provided procedure readily finds the optimal sequence (number and order) of such steps as well as the corresponding switching times. In most of the cases, however, the optimal trajectory does not follow the shape of known diafiltration techniques. Such non-linear α-control strategies can either be implemented through advanced control configuration or be simplified by a sequence of conventional process steps having a similar shape. The procedure allows one to quantify time and diluant savings of the optimal trajectory, thus, it is a useful engineering tool in the decision maker's hand.

We have demonstrated through selected case studies how one can apply the provided optimization theory. We have considered various, both theoretical and empirical, membrane response models as inputs for the given optimization procedure. A great deal of care is needed when generalizing the findings as far as general patterns in the shape of optimal trajectory are considered among different applications. This is due to the great variety and complexity of possible membrane response models regarding concentration-dependent rejections and flux functions. Note that the provided procedure is general in a sense that it can be readily applied to different membrane response models, but the computed optimal

profile may vary with the complexity of the membrane response model, the initial and final values, and the constraints involved in the model. We have shown that in many cases, time and diluant savings become more significant with increasing complexity of the model of membrane response, e.g. strongly non-linear membrane response with regard to both considered components.

Analysis and numerical optimization have shown that the optimal solution of the time minimization problem consists of usually three stages. The first and the last ones take extremal values of α which is pure concentration and either pure dilution (when α is unbounded from above) or operation with maximal α. The middle stage can have various time varying trajectories of control. Its complexity depends in the majority of studied cases on the functional dependence of the outflow q on concentrations. Often, if it is a function of macro-solute concentration only, the corresponding middle control strategy is constant macro-solute concentration maintaining operation (this is CVD if $R_1 = 1$) with various optimal concentrations of the macro-solute. This is shown in the examples with limiting flux and osmotic pressure models. There are also cases where the middle stage is VVD with $\alpha < 1$ as can be seen in the first treated case study. The most general form, however, is a complex non-linear curve (remaining case studies).

The problem of the minimization of the diluant consumption is analogous to the preceding case, but it depends only on the functional dependence of rejection coefficients on concentrations. The most usual case of constant rejection coefficients results in the so-called bang-bang control where only UF and pure dilution are allowed.

Results indicate that improvement of the proposed procedure as compared to traditional operation depends on the problem complexity. Processes with simpler membrane and/or permeate flow characteristics already operate near optimal regime. The improvement for more complex scenarios can be significant enough to invest in better models and advanced control configuration.

Chapter 7

Conclusions and Future Research

In this work we investigated optimal operation generalized batch diafiltration process. We have shown how to setup and treat the problem as a problem of optimal control (dynamic optimization). This results in specially structured input-affine optimal control problem. Because of this structure we were able to use analytical technique (Pontryagin's minimum principle) to follow necessary condition for optimality and derive structure of optimal control.

For the special, but rather common, class of processes with complete macro-solute rejection we characterized the optimal operation in the sense of optimal feedback law, i.e. optimal operation is characterized completely and uniquely. For general process we proposed numerical solution procedure which complexity is dramatically reduced in comparison with former optimal control problem.

We have critically discussed our findings and provided examples and case studies with varying order of complexity to illustrate how optimal operation of batch diafiltration processes can be found and to show advantages of optimal operation compared to traditional control techniques.

Motivation for future work can be summarized in three points:

1. Implementation of optimal operation on a real plant

   This will include using of robust and real-time optimization techniques in order to establish feedback control which rejects possible disturbances acting during the real process run.

2. Multi-objective dynamic optimization of batch diafiltration processes

Obviously, both studied optimal control problems (minimum time and minimum diluant problem) can be merged by considering optimal problem which objective function is written as a weighted sum of their objectives. These weights can directly represent costs to be paid for volume unit of diluant and cost for time unit of process run. Challenging task is to come up with solution which takes into account various weights (prices) and thus serve as a generalized form of solutions found in this study.

3. Extension of findings of this work to other filtration and membrane-supplied processes

   There are various process setups of filtration and diafiltration processes for which our findings are not applicable directly but similar approaches can be exploited in order to optimize performance of these processes. The same applies for other membrane-based processes such as membrane distillation, pervaporation, or processes where membrane reactors are involved.

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Author's Publications

Contribution of the author of this thesis to the field of dynamic optimization can be recognized following the list of his publications which is as follows:

- Articles in journals indexed in Current Contents Database

    1. Paulen, R. – Fikar, M. – Foley, G. – Kovács, Z. – Czermak, P.: Optimal feeding strategy of diafiltration buffer in batch membrane processes, Journal of Membrane Science, vol 411-412, pp. 160-172, 2012.
    2. Foley, G. – Paulen, R. – Fikar, M. – Kovács, Z. – Czermak, P.: Comments on "Diafiltration under condition of quasi-constant membrane surface concentration" by R. Field [J. Membr. Sci. 383 (1-2) (2011) 301-302]. Journal of Membrane Science, vol. 390-391, pp. 285-285, 2012.
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- Articles in domestic journals

    1. Paulen, R. – Fikar, M. – Latifi, M. A.: Dynamic Optimization of a Hybrid System: Emulsion Polymerization Reaction. Journal of Cybernetics and Informatics, vol. 10, pp. 31-40, 2010.

2. Paulen, R. – Fikar, M. – Čižniar, M. – Latifi, M. A.: Global Optimization for Parameter Estimation of Dynamic Systems. AT&P Journal Plus, no. 2, pp. 71-78, 2009.

- Articles in international conference proceedings

1. Paulen, R. – Benyahia, B. – Latifi, A. – Fikar, M.: Dynamic Simulation of Hybrid Differential Algebraic Systems Using gPROMS: Case Study in Emulsion Polymerization, In Proceedings of the 10th International Scientific – Technical Conference Process Control 2012, University of Pardubice, Kouty nad Desnou, Czech Republic, *accepted*.
2. Jelemenský, M. – Petáková, L. – Paulen, R. – Fikar, M.: Comparative Study in Dynamic Optimization of Emulsion Polymerization Reactor, In Proceedings of the 10th International Scientific – Technical Conference Process Control 2012, University of Pardubice, Kouty nad Desnou, Czech Republic, *accepted*.
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6. Paulen, R. – Fikar, M. – Kovács, Z. – Czermak, P.: Optimal Control of Diafiltration Process for Albumin Production. In Preprints of the 18th IFAC World Congress Milano (Italy) August 28 – September 2, 2011, pp. 14007-14012, 2011.
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Curriculum Vitae

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Education

- B.S. Food and Biochemical Technology, Slovak University of Technology, 2006.
  - *Minors*: Process Control and Chemical Engineering.
- M.A. Process Control, Slovak University of Technology, 2008
  - *Minor*: Dynamic Optimization
  - *Awards*: Slovak Chemical Society award for outstanding quality of diploma thesis
  - *Advanced study*: Global Dynamic Optimization at Lorraine Institute of Technology, Nancy, France, November 2007 – April 2008
- Ph.D. Process Control, Slovak University of Technology, *expected* 2012
  - *Majors*: Dynamic and Global Optimization

– *Minors*: Optimal Control of Membrane Processes, Hybrid Systems Modeling and Control

– *Awards*: award for outstanding quality of poster presentation at PERMEA 2010

– *Advanced Study*:

– study of global optimization at Lorraine Institute of Technology, Nancy, France, September – November 2008

– study of optimal process control at NTNU,Trondheim, Norway, May – June 2010

– study of dynamic optimization at Lorraine Institute of Technology, Nancy, France, September 2011 – February 2012

– study of global dynamic optimization at Imperial College London, London, UK, March – August 2012

Research Fields

- Deterministic Global and Dynamic Optimization, Model Predictive Control, Hybrid Systems, Optimization and Control, Membrane Processes, Polymerization Processes

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Computer Skills

- C/C++, Fortran, Windows, Unix/Linux, Siemens Simatic, Foxboro, Matlab, Simulink, gPROMS, MS Office, LaTeX, PHP, HTML, XML

Language Skills

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Resumé

Predkladaná dizertačná práca pojednáva o hľadaní optimálneho riadenia vsádzkových diafiltračných procesov. Diafiltrácia je membránový filtračný proces založený oddeľovaní rozpustených zložiek z roztoku na základe rozdielnej veľkosti častíc týchto zložiek. Uvažujeme kvapalné roztoky, ktoré obsahujú rozpúšťadlo, ktorým je spravidla voda, a rozpustené zložky. Cieľom procesu diafiltrácie je koncentrovať v roztoku hodnotné zložky, charakterizované väčšou veľkosťou častíc a vyššou molekulovou hmotnosťou a zároveň odstrániť balastné zložky, nečistoty s menšou molekulovou hmotnosťou a veľkosťou častíc. Procesy tohto typu sa využívajú najčastejšie vo farmaceutickom a potravinárskom priemysle a v biotechnologických aplikáciách.

V tejto práci skúmame vsádzkový diafiltračný proces (schematicky znázornený na obrázku 4.2), čo znamená, že spracovávaný roztok je vo svojom počiatočnom objeme na začiatku celej operácie prítomný v nádrži. Z tejto je postupne privádzaný k membránovému modulu. V tomto module sa nachádza polopriepustná membrána, ktorá je navrhnutá a vyrobená tak, aby zadržala čo najväčšie množstvo hodnotných zložiek (makrozložiek) roztoku a aby prepustila (odfiltrovala) čo najväčšie množstvo balastných látok. Relatívne množstvo zložky zadržané v roztoku je vyjadrené cez koeficient odporu membrány k tejto zložke. Z predchádzajúceho je zrejmé, že najčastejšie sa stretávame s prípadom úplného zadržania makrozložiek, ich koeficient odporu je 100% a naopak koeficient odporu balastných látok je nula. Často však môže nastať situácia, keď tieto koeficienty závisia od ostatných faktorov, najbežnejšie od koncentrácii jednotlivých zložiek vo filtrovanom roztoku.

Časť filtrovaného roztoku, ktorá nie je prepustená cez membránu, je kontinuálne odvádzaná späť do nádrže, kde sa mieša so zvyškom práve nefiltrovaného roztoku. Slučka

nádrž-membrána-nádrž je udržovaná pri konštantnom tlaku. Takéto riadenie je šetrné voči používanej membráne a zároveň stabilizuje systém od vonkajších vplyvov. Filtrát, časť filtrovaného roztoku prepustená cez membránu, je odvádzaný zo systému. Jeho objemový prietok cez membránu môže byť určený ako funkcia koncentrácii jednotlivých zložiek roztoku. Podobne, ako v prípade koeficientu odporu membrány k určitej zložke, aj prietok filtrátu cez membránu môže byť opísaný matematickým modelom, ktorý môže vychádzať z rýdzo teoretických, experimentálnych alebo teoreticko-empirických poznatkov.

Ako už bolo spomenuté, cieľom diafiltrácie je koncentrovať v roztoku požadované látky a vymyť nečistoty. Z praktického pohľadu možno hovoriť o dosiahnutí požadovanej koncentrácie makrozložky a nečistôt na konci operácie. Keďže koeficienty odporu ako aj prietok filtrátu sú funkciou koncentrácii zložiek prítomných v roztoku, proces diafiltrácie môže byt' riadený pridávaním rozpúšťadla na ovplyvňovanie týchto koncentrácii. Vhodnou voľbou riadiacej veličiny je túto zvolit' ako pomer prietokov pridávaného rozpúšťadla a filtrátu. Takáto veličina je bezrozmerová a tradične sa označuje symbolom α. Existujú viaceré tradične používané postupy nastavovania hodnôt tejto veličiny počas priebehu procesu. Tieto sú načrtnuté na obrázku 4.3. Cieľom tejto práce je nájsť optimálne riadenie procesu a určiť mieru suboptimality tradičných prístupov.

Nájsť optimálne riadenie procesu diafiltrácie znamená nájsť dynamický (časovo závislý) priebeh trajektórie $\alpha(t)$, ktorý minimalizuje:

1. dĺžku operácie (čas),

2. spotrebu pridávaného rozpúšťadla,

potrebnú na dosiahnutie stanoveného separačného zámeru. Táto práca sa teda venuje dvom problémom, ktoré môžu byt' formulované ako úlohy optimálneho riadenia v otvorenej riadiacej slučke, dynamickej optimalizácie.

Riešenie problému optimálneho riadenia znamená nachádzanie optimálnych trajektórii riadiacich a riadených veličín (stavov procesu). Toto predstavuje vo všeobecnosti veľmi zložitý matematický problém. Existujú však metódy, pomocou ktorých sa táto úloha dá vyriešit' analyticky. Tieto metódy zahŕňajú variačný počet, dynamické programovanie a princíp minima. Sú postavené na princípe určovania kandidátov pre optimálne riadenie na základe riešenia podmienok optimality problému optimálneho riadenia. V predkladanej práci využívame metódu ruského matematika L.S. Pontrjagina, princíp minima, ktorá ekvivalentne definuje problém optimálneho riadenia ako problém minimalizácie Hamiltoniánu.

Tento predstavuje špeciálnu funkciu, ktorá v sebe zahŕňa optimalizačné kritérium i matematický opis dynamiky procesu, model procesu.

Často sa však môžeme stretnúť so situáciou, keď nie je možné na základe podmienok optimality určiť optimálne riadenie, napríklad z dôvodu zvýšenej zložitosti problému, S rozvojom digitálnych počítačov sa preto postupne v praktických aplikáciách začali využívať metódy numerické. Tieto pracujú na princípe diskretizácie (aproximácie) buď pôvodného problému optimálneho riadenia alebo podmienok optimality. Medzi tieto metódy patria iterácia vektora riadenia, iterácia hraničnej podmienky, úplná parametrizácia, parametrizácia vektora riadenia a metóda viacnásobného nástrelu. Najviac je v práci využitá metóda parametrizácie vektora riadenia, ktorá transformuje problém optimálneho riadenia na problém nelineárneho programovania pomocou polynomických aproximácii trajektórii riadiacich veličín. Predkladaná práca taktiež uvádza prehľad metód získavania gradientov k dynamickým premenným, kde sa využívajú metódy konečných diferencií, citlivostných rovníc a adjungovaných premenných. Týmto sú predstavené hlavné praktické aspekty použitia numerických metód dynamickej optimalizácie.

Matematický model skúmaného procesu diafiltrácie je tvorený sústavou obyčajných diferenciálnych rovníc. Jeho štruktúra je taká že riadiaca veličina $\alpha(t)$ vystupuje v týchto rovniciach lineárne. Túto špeciálnu štruktúru model procesu využívame pri nájdení optimálneho riadenia. Keďže rovnako platí, že minimalizovaná účelová funkcia je lineárna v premennej $\alpha(t)$, Pontrjaginov princíp minima hovorí, že optimálne riadenie bude buď saturované na obmedzeniach, alebo bude dané takzvaným singulárnym riadením, alebo ich vzájomnou kombináciou. Bežne saturované riadenie predstavuje takzvaný koncentračný režim, v ktorom nepridávame do systému žiadne rozpúšťadlo, respektíve takzvaný zrieďovací režim, kde v jednom momente pridáme určité množstvo rozpúšťadla. Singulárne riadenie vyplýva z podmienok optimality a môže byť získané ako funkcia koncentrácii rozpustených zložiek.

Vo všeobecnom prípade diafiltračného procesu (ak predpokladáme ľubovoľnú závislosť koeficientov odporu membrány a prietoku filtrátu na koncentráciách jednotlivých filtrovaných zložiek) nemáme žiadnu informáciu o tom, kedy aplikovať saturované či singulárne riadenie. Optimálne riadenie však môžeme nájsť pomocou numerickej optimalizácie, ktorá určí poradie a časové trvanie jednotlivých úsekov riadenia, prípadne množstvo pridaného rozpúšťadla pre zrieďovací režim.

Ako už bolo spomenuté, často sa vyskytujúcou konštrukčnou vlastnosťou membrán

je ich konštantný úplný odpor k prepúšťaniu makrozložiek. V tomto prípade je možné nájsť analytické vyjadrenie krivky v priestore koncentrácii, pozdĺž ktorej je nutné použiť singulárne riadenie. Naviac je možné z umiestnenia tejto krivky a polohy bodu vyjadrujúceho aktuálne koncentrácie v systéme určiť, či je potrebné použiť riadenie saturované na minime či maxime. Optimálne riadenie diafiltračného procesu je teda exaktne určené sledovaním vývoja koncentrácii v systéme a je dané ako trojkroková operácia pri ktorej sa:

1. použije koncentračný alebo zrieďovací režim na prevedenie koncentrácii z počiatočného stavu na singulárny povrch (krivku)

2. vykoná dynamické pridávanie rozpúšťadla tak, aby sa bod predstavujúci aktuálne koncentrácie pohyboval po singulárnej krivke

3. záverečným krokom je opäť použitie saturovaného riadenia na dosiahnutie požadovaného koncového bodu v priestore koncentrácii

V predkladanej práci ďalej uvádzame niekoľko príkladov prevzatých z literatúry týkajúcej sa diafiltračných procesov. Postupne ukazujeme ako nájsť optimálne riadenie diafiltračného procesu popísaného modelmi, ktoré majú základ v teórii prestupu látky, modelmi s empirickými korekciami teoreticky odvodených modelov až po modely, ktorých štruktúra je získaná experimentálne. Tieto príklady a prípadové štúdie navyše ukazujú suboptimalitu tradičných postupov riadenia membránových diafiltračných procesov, pričom miera suboptimality narastá so zvyšujúcou sa komplexnosťou modelu použitej membrány. Ďalšou dôležitou črtou optimálneho riadenia sa ukazuje byť zvýšená zložitosť riadiaceho obvodu procesu operujúceho v optimálnom režime. Je teda namieste porovnať mieru suboptimality tradične riadenej diafiltrácie a určiť, či sa investícia do zložitejšej štruktúry riadenia vyplatí. Neprehliadnuteľným pozorovaním je taktiež časté dosahovanie koncentrácii, ktoré sú blízko hraniciam vyšetrovanej oblasti koncentrácii pri experimentálnom získavaní modelov. Zistenia uvedené v tejto práci teda dávajú informáciu o možnom postupe experimentátorom pracujúcim na experimentálnom hľadaní modelov skúmaných procesov.

Rozšírenie a ďalšie pokračovanie tejto práce spočíva v:

1. implementácii optimálneho riadenia na reálnom zariadení

2. multikriteriálnej optimalizácii vsádzkových diafiltračných procesov

3. aplikácii teoretických zistení pri skúmaní rôznych pokročilých filtračných procesov a procesov využívajúcich membránovú separáciu