

Heat Balance Calorimetry and Multirate State Estimation Applied to Semi-Batch Emulsion Copolymerisation to Achieve Optimal Control

Zur Erlangung des akademischen Grades eines

Dr.-Ing.

vom Fachbereich Bio- und Chemieingenieurwesen
der Universität Dortmund
genehmigte Dissertation

von

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aus
Osnabrück

Tag der mündlichen Prüfung: 30. September 2005

1. Gutachter: Prof. Dr. S. Engell
2. Gutachter: Prof. Dr. J. M. Asua

Dortmund, 2005

Schriftenreihe des Lehrstuhls für Anlagensteuerungstechnik
der Universität Dortmund (Prof.-Dr. Sebastian Engel)

Band 3/2005

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**Heat Balance Calorimetry and Multirate State
Estimation Applied to Semi-Batch Emulsion
Copolymerisation to Achieve Optimal Control**

D 290 (Diss. Universität Dortmund)

Shaker Verlag
Aachen 2005

Bibliographic information published by Die Deutsche Bibliothek

Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the internet at <http://dnb.ddb.de>.

Zugl.: Dortmund, Univ., Diss., 2005

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Printed in Germany.

ISBN 3-8322-4589-8
ISSN 0948-7018

Shaker Verlag GmbH • P.O. BOX 101818 • D-52018 Aachen
Phone: 0049/2407/9596-0 • Telefax: 0049/2407/9596-9
Internet: www.shaker.de • eMail: info@shaker.de

Acknowledgments

Nobody works alone and nobody can manage a large piece of work all by himself. I was very fortunate to be able to rely on a large number of friends, colleagues and members of my family for continuous support and understanding.

This thesis is the result of my five year stay at the Chair of Process Control, Department of Biochemical and Chemical Engineering, University of Dortmund. The holder of the chair, Prof. Sebastian Engell, gave me the chance in 1998 to embark on this project. During our long working relationship, Prof. Engell always supported my work and was always available for fruitful discussion on the work's progress. This support and his always helpful advice I wholeheartedly acknowledge. I would also like to thank Prof. Sadowski and Prof. Agar for being members of my PhD exam committee.

During my research, I spent seven months at POLYMAT in San Sebastian, Spain. Apart from the nicer sides of life in northern Spain, the stay was also professionally very productive largely due to the good discussion and support of Prof. Asua (head of POLYMAT), who also agreed to co-referee this thesis and of Prof. Leiza, who spent a lot of time with me explaining patiently all the questions I had on emulsion polymerisation.

The work published in this thesis is only part of a larger research project on emulsion polymerisation going on at the Chair of Process Control. This is why a lot of ideas were the results of discussions. All of the fruitful discussions and initiatives on future work directions I had with Dr. Ralf Gesthuisen, at the time senior researcher at the group. Without his professional help and his friendship none of this would have been possible and I am greatly indebted to him. The other members of the group, Sachin Arora, Mehdi Rajabi and Wolfgang Mauntz as well as our technician Wolfgang Brozska all provided valuable help.

There were also a number of students who participated in this work through projects and student jobs. Anne Hölscher, Meik Franke, Dirk Nitschke, Hakan Fis and Gerrit Niggemann all played their part.

The larger circle of people at the Chair of Process Control also helped me and many other people to get this far. There are our secretaries, Gisela Hensche and Dorothea Weber who are always quick to help and know all the important non-technical issues of university life. There are my colleagues and friends Goran Frehse and Kai Dahde who as electrical engineers always helped with control problems, Michael Wieland who provided great mathematical support and Manuel Remelhe whose outstanding knowledge in chemical engineering and modelling makes him a bonus in any discussion.

My stay in San Sebastian would not have been a success without Loli Jañez and Felipe Alarcia. Without you guys I wouldn't have survived. My good friend from student days Alex Allen, proof-read this thesis for me.

Last but not least, there is the moral support. My wife Britta Zeumer was always there for me. Her support was required for me to go on. I was also always sure of the continuous support of my mother Waltraud and her partner Hermann and my brother Matthias and his girl-friend Corinna.

There are many more friends and colleagues who supported me and if your name does not appear here, don't think I am not grateful. My deepest thanks go to everybody who supported me over the last 7 years.

Thank you, all of you!

Abstract

Rising demands for optimal production, better product quality and shorter batch times require ever improving process operation in the chemical industry. Batch and semi-batch processes form a large part of the production and often exhibit optimisation potential. For optimal operation, measuring or estimating product quality variables is a requirement, otherwise online optimisation is not possible. Polymerisation processes are amongst the most difficult as temperature measurements are available frequently during a batch, many product quality indicators, however, cannot be measured online or only with time delay. Emulsion copolymerisation is a multiphase process, where the concentration of the monomers in the reaction loci cannot be measured at all. Additionally, emulsion polymers are out of the tank products, with little or no downstream processing. Therefore, the actual reactor operation is the single most important step in maintaining product quality.

It is the aim of this thesis to present possible cornerstones of an optimal control concept of emulsion polymerisation processes and to tie them together in an example of optimal control.

The solid basis of the application of optimal operation is a mathematical simulation model of the process and relevant reduced models. Using literature models to develop a kinetic model, which is validated by experimental data and reduced by sensitivity analysis of submodels, this basis is formed.

Process states which are difficult to measure can often be reconstructed using easily measured states and mathematical models within state estimation schemes. If additional measurements are available at different sampling rates or longer time delay classic estimation schemes need to be extended to cover all available measurements.

Multirate state estimation schemes are discussed and new approaches are developed. Based on known techniques such as the Moving Horizon Estimator (MHE), a promising new multirate state estimation scheme, the Multirate Moving Horizon Estimator (MMHE) is considered.

The developed MMHE is applied to estimate the concentration of the monomers in the reaction loci of emulsion copolymerisation. Its fixed structure allows for computation time optimisation by turning it into a Constrained Extended Kalman Filter, which can still use the available delayed measurements.

Calorimetry is investigated to better understand the equipment, typically a jacketed tank. It is used to estimate the heat transfer coefficient between the jacket and the tank in a jacketed reactor during the batch.

In emulsion copolymerisation a large number of factors influence the process and the final product, only some of which can be influenced and even fewer used as manipulated variables. State estimation provides information about the ongoing process and optimisation based control uses this information to run the process to obtain optimal results in minimal time.

A novel control scheme is applied to emulsion polymerisation using the estimated states achieving time optimal operation by running the process along limiting constraints. While producing a polymer with desired molecular weight properties, the estimation of the heat transfer coefficient allows the scheme to remain time optimal for all process conditions as maximum heat removal is guaranteed.

Zusammenfassung

Die Situation der chemischen Industrie verlangt nach optimaler Produktion und besserer Produktqualität. Daher muss die Prozessführung weiterhin verbessert werden. Chargenprozesse sind ein wichtiger Bestandteil der Produktion und zeigen häufig Optimierungspotenzial. Um diese Optimierung auch online durchzuführen, müssen Qualitätsgrößen bekannt sein. Bei Polymerisationsprozessen ergeben sich besondere Schwierigkeiten, da während einer Charge Temperaturmessungen normalerweise regelmäßig vorhanden sind, viele Qualitätsgrößen jedoch nicht online verfügbar sind. Bei der Emulsionspolymerisation kann die Monomerkonzentration in den Reaktionsorten aufgrund der Mehrphasigkeit des Prozesses überhaupt nicht gemessen werden. Zusätzlich sind Emulsionspolymere häufig Produkte, die keinen weiteren Verfahrensschritten unterliegen, daher ist die Prozessführung des Polymerreaktors der wichtigste Schritt zur Erreichung der gewünschten Produktqualität.

Es ist das Ziel dieser Arbeit, die Eckpfeiler für ein optimales Regelungskonzept der Emulsionspolymerisation vorzustellen und ein daraus entwickeltes Konzept in einem Beispiel zu erläutern.

Die Basis für eine optimale Prozessführung stellt ein mathematisches Simulationsmodell des Prozesses dar. Außerdem benötigt man vereinfachte Modelle für Optimierung und Regelung. Auf Basis von Literaturmodellen wird ein kinetisches Modell entwickelt, welches mit experimentellen Daten validiert und mit Hilfe der Sensitivitätsanalyse von Untermodellen vereinfacht wird.

Prozesszustände, welche schwer zu messen sind, können oft mit Hilfe von leicht zu messenden Zuständen und einem mathematischen Modell durch Zustandsschätzer rekonstruiert werden. Falls weitere Messungen mit verschiedenen Abtastraten oder mit Messverzögerung zur Verfügung stehen, müssen die klassischen Zustandsschätzverfahren erweitert werden, um all diese Messungen nutzen zu können.

Zustandsschätzverfahren für Messungen mit verschiedenen Abtastraten werden diskutiert und ein neuer Ansatz wird entwickelt. Basierend auf dem bekannten Verfahren des Zustandsschätzers auf bewegtem Horizont (Moving Horizon Estimator - MHE) wird eine neue Zustandsschätzer entwickelt, der Zustandsschätzer auf bewegtem Horizont für Messungen mit verschiedenen Abtastraten (Multirate MHE - MMHE).

Der entwickelte MMHE wird eingesetzt, um die Monomerkonzentrationen in den Reaktionsorten der Emulsionscopolymerisation zu schätzen. Durch den Einsatz einer festen Struktur entsteht ein effizientes beschränktes erweitertes Kalman Filter, welches weiterhin alle Messungen nutzt. Kalorimetrie wird zusätzlich angewandt, um den Wärmeübergang in den genutzten Rührkesseln zu schätzen.

In der Emulsionspolymerisation werden das Produkt und der Prozess durch eine große Anzahl Faktoren beeinflusst, von denen nur wenige von außen eingestellt werden können. Durch Zustandsschätzung erhält man Informationen über vorher nicht bekannte Zustände, die in einem optimalen Regelungskonzept eingesetzt werden können, um die Chargenlänge zu minimieren. Ein neues Regelungskonzept wird entworfen, welches die zeiotoptimale Fahrweise unter Einhaltung der Produktqualität garantiert, indem an aktiven Beschränkungen gefahren wird. Mit dem Konzept kann eine beliebige Molekulargewichtsverteilung zeiotoptimal hergestellt werden.

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Nomenclature

The following general nomenclature is used throughout this work:

- Roman-boldface (Example \mathbf{x} or \mathbf{A}) denotes a vector or a matrix.
Capital letters denote matrices, lowercase letters denote vectors.
- $\lfloor \cdot \rfloor$ denotes the nearest smaller integer value.
- $\lceil \cdot \rceil$ denotes the nearest larger integer value.
- $\| \cdot \|$ denotes a norm. For vectors the Euclidian norm is assumed, for matrices the norm is the largest singular value.
- $[\cdot]$ denotes concentration.

Abbreviations

BA	Butyl Acrylate
BuM	Butyl Maleate
CEKF	Constrained Extended Kalman Filter
CMC	Critical Micelle Concentration
CSTR	Continuous Stirred Tank Reactor
CTA	Chain Transfer Agent
DUO	Distance to Unobservability
EKF	Extended Kalman Filter
KF	Kalman Filter
GPC	Gel Permeation Chromatograph
MHE	Moving Horizon Estimator
MMA	Methyl Methacrylate
MMHE	Multirate Moving Horizon Estimator
MWD	Molecular Weight Distribution
PDI	Polydispersity Index

PFR	Plug Flow Reactor
PLP	Pulsed Laser Polymerisation
PSD	Particle Size Distribution
QSSA	Quasi Steady State Approximation
SECP	Semicontinuous Emulsion Co-Polymerisation
VA	Vinyl Acetate

Roman Letters

Symbol	Explanation	Unit
A	system matrix in state space system description	
<i>A</i>	heat transfer area	m^2
<i>a</i>	multirate estimation improvement factor	
<i>a</i>	surface area of one particle (Smith and Ewart)	
A_B	bottom area of the vessel	m^2
A_{\max}	maximum jacket area	m^2
A_B	base area of the tank	m^2
B	control matrix in state space system description	
<i>b</i>	channel width	m
\mathbf{B}_0	matrix of collocation coefficients at $\tau = 0$	
\mathbf{B}_p	matrix of collocation coefficients at τ_i	
C	measurement matrix in state space system description	
\bar{c}	average termination rate coefficient	$1/\text{s}$
<i>c</i>	molecular termination rate constant	1s
$c_{p,R}$	heat flow capacity of the reactor content	W/K
c_p	heat flow capacity of the jacket content	W/K
C_A	concentration of species <i>A</i>	kmol/m^3
CMC	critical micelle concentration	kmol/m^2
c_p	fluid heat capacity of the jacket mass flow	J/kgK
$c_{p,R}$	fluid heat capacity of the reactor content	J/kgK
C_R	total heat capacity of the reactor and its contents	W

ΔH_R	enthalpy of chemical reaction	kJ/kmol
\mathbf{D}	punch-through matrix in state space system description	
D_i^h	diffusion coefficient of radicals in the hairy layer	mol/m ² s
D_i^w	diffusion coefficient of radicals in water	mol/m ² s
D_i^p	diffusion coefficient of radicals of type i particle phase	
d_R	diameter of the reactor	m
Δt	sampling period	s, min
\mathbf{e}	(estimation) error vector	
E	expected value	
E_A	activation energy	J/mol
E_A	activation energy of A	J/mol
\mathbf{F}	function vector sampled nonlinear state space model	
\mathbf{f}	function vector (returns a vector)	
\mathbf{f}	function vector continuous nonlinear state space model	
f	function	
f	initiator decomposition rate efficiency factor	
f_G	scaling factor of the reactor	
\mathbf{f}_x	Jacobian matrix of function \mathbf{f} w.r.t. \mathbf{p}	
F_p	absorption efficiency (adjustable)	mol/m ² s
Φ_p^p	volume fraction of polymer in particle phase	
\mathbf{f}_x	Jacobian matrix of function \mathbf{f} w.r.t. \mathbf{x}	
\mathbf{f}_z	Jacobian matrix of function \mathbf{f} w.r.t. \mathbf{z}	
h	channel height	m
h_R	liquid height of the reactor	m
$h_{R,\max}$	reactor height	m
\mathbf{I}	identity matrix	
I	initiator	
$[I]^F$	initiator concentration in the feed solution	mol/l
$[i]^j$	concentration of species i in phase j	mol/l

$[I]^w$	initiator concentration in the water phase	mol/l
J	objective function	
j	complex operator	
\mathbf{K}	state estimator gain matrix	
k	heat transfer coefficient	W/m ² K
k_0	particle desorption (Smith and Ewart)	m·part/s
k_0	reaction rate constant	m ³ /s
k_{0i}	constant of the diffusional exit rate of a radical of type i	
k_A	reaction rate coefficient of first order reaction of A	1/s
k_a	particle absorption rate coefficient	1/s
k_d	radical desorption rate coefficient	1/mol
k_I	initiator decomposition rate coefficient	1/s
k_d	particle desorption rate coefficient	1/s
k_f	chain transfer rate coefficient	1/mols
k_{fij}	chain transfer rate coefficient	
k_{fX}	chain transfer rate coefficient	1/kmols
k_i^d	Partition coefficient species i between droplet and water phase	
k_i^p	Partition coefficient species i between particle and water phase	
k_{pij}	reaction rate coefficient of radical j reacting with monomer i	mol/s
k_T	termination rate coefficient	1/mols
k_{Tij}	termination rate coefficient	
k_t^w	termination rate in the water phase	
L	length of the lower part of the jacket	m
L_{\max}	total jacket length	m
\dot{m}	'real' mass flow through the jacket	kg/s
\tilde{M}^{\cdot}	Polymeric radicals	
M	molecular weight	g/mol
m	mass in the jacket	kg
$[\sim M^j \cdot]$	concentration of polymer radicals	mol/l

M_M	molecular weight of the monomer	g/mol
\bar{M}_n	instantaneous normalised number average chain length	
$M(n)$	chain length distribution function, number of chains of length n	
M_n	instantaneous number average chain length	
m_R	mass of the reactor content	kg
$\dot{m}_{R,\text{in}}$	mass flow of the feed	kg/s
\dot{m}_{set}	set mass flow through the jacket	kg/s
\overline{M}_w	molecular weight average normalised molecular weight	
M_w	molecular weight average molecular weight	
\mathcal{N}	normal distribution	
\bar{n}	average number of radicals per particle	
N	horizon length of the moving horizon estimator	
N	total number of particles (Smith and Ewart)	
n	length of a polymer chain	
n	number of free radical in a particle (Smith and Ewart)	
n	number of moles	mol
N_A	Avogadro's number	$6.022 \cdot 10^{23}$ part/mol
N_i	number of particles with i radicals	
n_I	number of moles of initiator	mol
\dot{n}_M	molar feed rates of monomer	mol/s
n_M	number of moles of monomer in the system	mol
N_P	particle concentration in the system	part/l
n_{R^w}	moles of radicals in the water phase	mol
N_T	absolute number of particles in the system	
N_T	number of particles	
n_M^T	total amount of monomer to be fed	mol
n_X^T	total amount of CTA to be fed	mol
\dot{n}_X	molar feed rates of CTA	mol/s
n_X	number of moles of CTA in the system	mol

P	covariance matrix of the estimation error	
p	parameter vector	
<i>P</i>	probability	
<i>p</i>	number of internal collocation points	
\dot{Q}	energy flow or power	kW
\dot{Q}_{in}	heat flow into the jacket	W
\dot{Q}_J	conductive heat flow through reactor wall	W
\dot{Q}_{out}	heat flow out of the jacket	W
$\dot{Q}_{R,in}$	heat flow of the feed	W
$\dot{Q}_{R,out}$	heat flow out of the reactor	W
$\dot{Q}_{R,loss}$	heat loss of the reactor	W
$\dot{Q}_{R,source}$	heat of reaction	W
Q	covariance matrix of the state noise	
<i>Q</i>	energy	J
Q_B	observability matrix	
R	covariance matrix of the measurement noise	
<i>r</i>	reaction rate	mol/s
<i>R_G</i>	universal gas constant	8.314 J/molK
<i>r_p</i>	radius of one particle	m
<i>r_M^p</i>	reaction rate of monomer in the particle phase	mol/s
<i>r_X^p</i>	reaction rate of CTA in the particle phase	mol/s
<i>r_T^p</i>	total termination rate	mol/s
[<i>R</i>] ^w	concentration of radicals in the water phase	mol/l
S	scaling matrix, with index sensitivity matrix	
S	sensitivity matrix	
s	vector of slopes needed for finite element placement	
<i>SS</i>	steady state	
S_z	sensitivity matrix to algebraic variables z	
<i>T</i>	Temperature	K

T	time	s, min
t	time	s, min
T_J	temperature in the jacket	K
T_R	temperature in the reactor	K
T_0	initial temperature	K
$T_{J,\text{in}}$	jacket inlet temperature	K
$T_{J,\text{out}}$	jacket outlet temperature	K
$T_{R,\text{in}}$	temperature of the feed stream	W
T_{x_0}	initial temperature at every location coordinate of the jacket	K
t_d	time delay or dead time	s, min
T_g	glass transition temperature	K
T_S	sampling period	s, min
\mathbf{u}	vector of inputs or manipulated variables	
\dot{V}	liquid flow through the jacket	m^3/s
$\dot{V}_{R,\text{in}}$	feed flow into the reactor	m^3/s
$\dot{V}_{R,\text{out}}$	flow out of the reactor	m^3/s
\dot{V}	volumetric flow or feed rate	$1/\text{s}$
V	liquid hold up in the jacket	m^3
V	volume of reactor contents	l
v	volume of one particle (Smith and Ewart)	l
V^R	liquid hold up in the reactor	m^3
V^d	total droplet phase volume	l
\dot{V}_E	emulsifier solution addition rate	$1/\text{s}$
V_F	free volume	
\dot{V}_I	feed of initiator solution	$1/\text{s}$
\dot{V}_I	initiator solution addition rate	$1/\text{s}$
\underline{V}_i	molar volume of species i	$1/\text{mol}$
V_i	total volume of species i in the system	l
V_i^d	droplet phase volume of species i	

V_i^p	particulate phase volume of species i	l
V_i^w	water phase volume of species i	l
V^p	volume of the particulate phase	l
v_p	volume of one particle	
V_{Pol}^p	volume of polymer in the polymer phase	l
\dot{V}_W	water addition rate	l/s
V^w	volume of the water phase	l
V_W	is the volume of water in the system	l
$\dot{\bar{V}}_W$	overall feed rate of water	l/s
\mathbf{W}	noisy weighting matrix	
\mathbf{W}	weighting matrix	
$\overline{W}(n)$	instantaneous normalised molecular weight distribution	
$W(n)$	instantaneous molecular weight distribution	
$\overline{W}_T(n)$	total (accumulated) normalised molecular weight distribution	
\mathbb{X}	set, here a set of state vectors	
X	conversion	
X_C	Current conversion of the given recipe	
$\hat{\mathbf{x}}$	estimated state vector	
\mathbf{y}	vector of outputs or measured variables	
Y_i	Fraction of monomer i in the polymer	
z	spatial distribution variable	

Greek Letters

Symbol	Explanation	Unit
α_{ij}	starting position of finite element j in superelement i	
$\Delta\alpha_{ij}$	length of finite element j in superelement i	
β_i	probability that a monomer or CTA radical reacts in the water phase	
δ	Dirac impulse	
δ_{ij}	Kronecker delta	
δ_1	thickness of the hairy layer	m

ϵ	mathematical epsilon, small value larger than zero	
φ	approximate solution of the first moment of the distribution N_i	
λ	eigenvalue	
μ_i	i th moment	
μ_i^j	i th moment of monomer j	
φ	measurement noise vector	
Ψ	Solution of a cost function	
ρ	fluid density of the jacket content	kg/m ³
ρ_R	fluid density of the reactor content	kg/m ³
ρ'	radical absorbtion (Smith and Ewart)	
ρ_{Pol}	density of the polymer	g/l
σ	singular value	
σ	standard deviation	
τ	integrand time	
τ	normalised time	
τ	residence time	s
$\Delta\xi_i$	length of superelement i	
ξ_i	starting position of superelement i	
ξ	state noise vector	

Indices

<u>Index</u>	<u>Explanation</u>
0	initial condition
bb	backbiting
c	continuous system
d	radical desorption
end	end of an interval
equip	equipment
F	free
f	chain transfer

fixed	fixed structure
i	i th element in a vector
i	monomer i
ij	matrix element row i and column j
in	input
Inh	inhibited
$inst$	instantaneous
k	counter
M^i	monomer i
NE	number of finite elements
NSE	number of superelements
P	polymer
p	polynomial interpolation
s	steady state
T	termination
var	variable structure
X	CTA

Superscripts

<u>Superscript</u>	<u>Explanation</u>
-1	Inverse of a matrix
d	droplet phase
p	droplet phase
F	fast mesurements
FS	fast and slow mesurements
I	initiator
p	particle or polymer phase
R	radicals
R	reactor
S	slow mesurements

S_T	surfactant
T	transposed
p	water phase
w	water phase