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Heiko Brandt

**Modeling, Process Monitoring and
Optimizing Control of Emulsion
Polymerization Processes**



**Modeling, Process Monitoring
and Optimizing Control of
Emulsion Polymerization Processes**

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Abstract

Emulsion polymerization is an important industrial (semi-) batch process for the production of latices, which are used as adhesives and paints. On the growing, but very competitive polymer market, a continuous process improvement is essential. Off-line perfectioning of the production recipes is a common way to increase plant productivity. But only the on-line application of optimizing control schemes enables the production of tailor-made polymer properties at the highest possible reaction rate that still allows tight temperature control and respects the safety constraints in presence of process disturbances. This topic is addressed in this work. Basis is a simulation model for a radical emulsion polymerization, which has been calibrated to the performance of styrene and butyl acrylate homo- and co-polymerizations. Using that model, the process observability and state estimation of emulsion polymerization processes with temperature measurements is analyzed and the performance of different Extended Kalman Filters is examined in presence of plant-model mismatches. The results show, that temperature measurements alone do not enable a robust estimation of the inner process states in a co-polymerization process. Therefore, the use of an additional ultrasound velocity measurements is discussed, motivated by the difference in the sound velocity of water, monomers, and polymer. As all available literature approaches to describe the sound velocity as a function of the mixture composition have their limitations, an own model is derived. Afterwards, the impact of temperature and sound velocity fusion on the estimator performance is examined, illustrating that the monitoring robustness versus kinetic parameter mismatches is improved. At last, different control schemes are tested for batch time minimization and production of desired co-polymer compositions. It is demonstrated that batch time reduction does not require model-based control, while a model-predictive control scheme to adjust the polymer properties does not improve the results of a classical PI control approach in the applied example.

Kurzfassung

Emulsionspolymerisation ist ein industriell häufig eingesetztes, halbkontinuierliches Verfahren zur Herstellung von Latexen. Diese finden unter anderem in Klebstoffen oder in Farben und Lacken Verwendung. Trotz des anhaltenden Wachstums des Polymermarktes ist dieser stark umkämpft. Eine stetige Prozessverbesserung ist daher unerlässlich. Ein häufig genutzter Ansatz zur Steigerung der Produktivität ist die offline Optimierung der eingesetzten Produktionsrezepte. Allerdings erlaubt nur die online Anwendung von optimierenden Regelungsschemata den Prozess trotz Prozessschwankungen bei maximaler Reaktionsrate zu fahren, dabei zeitgleich die gewünschten Polymereigenschaften einzustellen, ohne jedoch die Prozesssicherheit zu gefährden. Die Modellierung, Prozessverfolgung und Optimierung von Emulsionspolymerisationsprozessen wird in dieser Arbeit behandelt. Grundlage ist ein Simulationsmodell für eine radikalische Emulsionspolymerisation, das für die Beschreibung von Homo- und Co-Polymerisationen von Styrol und Butylacrylat parametrisiert wird. Aufbauend auf diesem Modell wird die Beobachtbarkeit und Zustandsschätzung von Emulsionspolymerisationsprozessen mit Hilfe von Temperaturmessungen analysiert und das Verhalten von verschiedenen erweiterten Kalman Filtern unter Modellfehlern getestet. Als Ergebnis zeigt sich, dass Temperaturmessungen allein keine robuste Schätzung der inneren Prozesszustände im Fall von Co-Polymerisationen erlauben. Daher wird ergänzend die Anwendung von Ultraschallmessungen diskutiert. Motiviert wird dies durch die großen Unterschiede zwischen den Ultraschallgeschwindigkeiten von Wasser, Monomer und Polymer. Da in der Literatur verfügbare Ansätze zur Beschreibung der Ultraschallgeschwindigkeit in Abhängigkeit der Zusammensetzung einer Mischung gewisse Limitierungen haben, wird ein eigener Modellansatz entwickelt. Ultraschall- und Temperaturmessungen werden im Anschluss zu einem kombinierten Sensorkonzept für die Zustandsschätzung zusammengeführt. Die Robustheit der Zustandsschätzung im Fall von Fehlern in den kinetischen Modellparametern wird dadurch deutlich verbessert. Als letztes werden verschiedene Regelungsschemata zur Reduktion der Batchzeiten und Einstellung der gewünschten Polymereigenschaften getestet. Dabei wird gezeigt, dass zur Reduktion der Batchzeiten kein modellbasierter Regelungsansatz benötigt wird, während ein prädiktiver Regelungsansatz zur Einstellung der Polymereigenschaften nicht zwingend eine bessere Leistung als ein klassischer PI-Regler bringt.

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ABBREVIATIONS

BA	Butyl Acrylate
CMC	Critical micelle concentration
CSTR	Continuous stirred tank reactor
CTA	Chain transfer agent
DACC	Droplet avoidance constrain controller
DAE	Differential algebraic equations
DCS	Distribution control system
DUO	Distance to unobservability
EKF	Extended Kalman Filter
ELO	Extended Luenberger Observer
I	Initiator molecule
JTCC	Jacket temperature constraint controller
KF	Kalman Filter
M	Monomer unit
MHE	Moving Horizon Estimator
MMA	Methyl Methacrylate
MPC	Model predictive control
MW	Molecular weight
MWD	Molecular weight distribution
NLP	Nonlinear programming problem
NMPC	Nonlinear model predictive control
PMMA	Poly Methyl Methacrylate
PID	Proportional-integral-derivative controller
PSD	Particle size distribution
PVAc	Poly Vinyl Acetate
QSSA	Quasi steady state approximation
$R^\bullet$	Free radical
RM_n	Dead polymer chain with degree of polymerization equal to n
$RM_n^\bullet$	Living polymer chain with degree of polymerization equal to n
SDS	Sodium dodecyle sulfate
STY	Styrene
TOC	Temperature oscillation calorimetry
TA	Transfer agent
VA	Vinyl Acetate

LATIN SYMBOLS

a_i	Gel effect parameter for monomer i	[-]
b	Parameter in the model of Siani	[-]
c	Sound velocity	[m/s]
c	Non-linear constraint	various
c_p	Heat capacity	[J/kg/K]
d	Disturbance vector	mixed
d_p	Particle diameter	[m]
d_{ind}	droplet indicator	[m ³]
e	Estimation error	mixed
e_j	j -th eigenvector	mixed
f	System model	mixed
f	Frequency	[Hz]
f	Efficiency of radical initiation	[-]
h	Measurement model	mixed
h	Reactor height	[m]
h	Sampling interval	[s]
k_a	Average radical absorption rate coefficient	[l/mol·s]
$\bar{k}_d$	Average radical desorption rate coefficient	[1/s]
k_{fii}^0	Frequency factor of the chain transfer rate	[l/mol·s]
k_{fij}	Chain transfer rate coefficients	[l/mol·s]
k_i^d	Partition coefficient of species i between droplet and water phase ..	[-]
k_i^p	Partition coefficient of species i between particle and water phase ..	[-]
k_A	Heat exchange coefficient	[W/K]
$\hat{k}_A$	Estimated heat exchange coefficient	[W/K]
kA_{loss}	Heat exchange coefficient to environment	[W/K]
k_I	Initiator decomposition rate coefficient	[1/s]
k_I^0	Frequency factor of the initiator decomposition rate	[1/s]
k_P	Propagation rate coefficient	[l/mol·s]
$k_{P_{ii}}^0$	Frequency factor of the propagation rate	[l/mol·s]
$\overline{k_{P_{ij}}}$	Propagation rate coefficient	[l/mol·s]
$\overline{k_{P_i}}$	Pseudo propagation rate coefficient	[l/mol·s]
k_T	Termination rate coefficient	[l/mol·s]
k_{Tc}	Termination rate coefficient by combination	[l/mol·s]
k_{Td}	Termination rate coefficient by disproportionation	[l/mol·s]
$k_{T0_{ii}}^0$	Frequency factor of radical termination rate	[l/mol·s]
$\bar{k}_T$	Average termination rate coefficient	[l/mol·s]
m	Mass	[kg]
m	Number of monomer species present	[-]
m	Number of measurements	[-]
$\dot{m}$	Mass flow	[kg/s]
n	Number of moles	[mol]

NOMENCLATURE

n	Number of differential process states	[-]
$\hat{n}$	Estimated number of moles	[mol]
n_i	Number of molecules with degree of polymerization i	[-]
$\dot{n}$	Molar feed	[mol/s]
$\bar{n}$	Average number of radicals per particle	[-]
$\hat{\bar{n}}$	Estimated average number of radicals per particle	[-]
p	Pressure	[Pa]
p	Parameter	various
p	Sound wave	[Pa]
p_0	Initial pressure amplitude	[Pa]
q	Element of the covariance matrix Q	various
r	Number of process inputs	[-]
r	Radius	[m]
r_{ij}	Reactivity ratio	[-]
r	Reaction rate	[kg/s]
$\hat{r}$	Estimated reaction rate	[kg/s]
r_p	Radius of the monodispers particles	[m]
s	Weighting factors in the co-polymerization ultrasound model	[-]
s	Sensitivity	various
t	Time	[s]
u	Input vector	mixed
$\bar{v}$	Molar volume	[l/mol]
x	Distance	[m]
x	Process state vector	mixed
$\hat{x}$	Estimated process state vector	mixed
y	Measurement vector	mixed
$\hat{y}$	Estimated measurement vector	mixed
A	System matrix	mixed
A	Heat exchange area	[m ²]
B	Input matrix	mixed
C	Measurement matrix	mixed
C_R	Heat capacity of the reactor	[J/K]
C_S	Heat capacity of the reactor and content	[J/K]
CC_i	fraction of co-polymer composition of monomer i by weight	[-]
D	Diffusion coefficient	[dm ² /s]
E	Disturbance input matrix	mixed
$[E]$	Concentration of emulsifier	[mol/l]
E_{fi}	Activation energy of chain transfer	[J/mol]
E_I	Activation energy of initiator decomposition	[J/mol]
$E_{P_{ii}}$	Activation energy of propagation	[J/mol]
$E_{T_{ii}}$	Activation energy of radical termination	[J/mol]
F_p	Absorption efficiency	[-]

H	Disturbance system matrix	mixed
ΔH_R	Reaction enthalphy	[J/mol]
I	Identity matrix	mixed
$[I]$	Concentration of initiator	[mol/l]
$[I^\bullet]$	Concentration of initiator radicals	[mol/l]
K	Correction gain	mixed
K_I	Controller gain (integral)	mixed
K_P	Controller gain (proportional)	mixed
M_i	Molecular weight of a molecule with degree of polymerization i	[g/mol]
MW	Molecular weight	[g/mol]
$\overline{M}_n$	Number average molecular weight	[g/mol]
$[M]$	Concentration of monomer	[mol/l]
$[\sim M^\bullet]$	Concentration of a monomer radical	[mol/l]
N_A	Avogadro constant	[1/mol]
N_C	Control horizon	[-]
N_n	Number of particles with n radicals	[-]
N_P	Concentration of particles	[particle/m ³]
N_P	Prediction Horizon	[-]
N_T	Absolute number of particles in the system	[-]
P	Covariance matrix for estimation error	mixed
P_n	Degree of polymerization	[-]
P_j	Probability that a certain radical has the endgroup M_j	[-]
Q	Heat	[J]
Q	Covariance matrix for model noise	mixed
$\dot{Q}$	Heat flow	[W]
$\dot{Q}_{Ex}$	Heat flow between reactor and jacket	[W]
$\dot{Q}_R$	Generated heat of reaction	[W]
$\hat{\dot{Q}}_R$	Estimated heat of reaction	[W]
$\dot{Q}_{loss}$	Heat flow to environment	[W]
R	Ideal gas constant	[J/mol·K]
R	Covariance matrix for measurement noise	mixed
R	Sound reflection	[-]
$[R]$	Concentration of radicals	[mol/l]
S	Sensitivity matrix	mixed
SC	Solid content	[-]
SC_{total}	Total solid content	[-]
SC_{Pol}	Solid content due to polymer generation	[-]
T	Temperature	[K]
T_N	Time constant	[s]
T_g	Glass transition temperature	[K]
$\hat{T}$	Estimated temperature	[K]
U	Voltage	[V]

NOMENCLATURE

V	Volume	$[m^3]$
$\hat{V}$	Estimated volume	$[m^3]$
$\dot{V}$	Volume flow	$[m^3/s]$
W	Weighting matrix	mixed
X_F	Conversion based on the recipe formulation	[-]
X_I	Conversion based on the fed reactant	[-]
X_R	Conversion based on the current feed flow	[-]
Y_i	Mole fraction of monomer i of co-polymer composition	[-]
$Y_{i,inst}$	Instantaneous co-polymer composition of monomer i	[-]
Z	Sound impedance	[-]
Z	Glass transition parameter in the model of Siani	[-]

Greek Symbols

α	Sound attenuation	$[dB/cm]$
α	Volume expansion coefficient	$[1/K]$
β	Adiabatic compressibility	$[m^2/N]$
$\Delta\beta$	Non-ideal compressibility parameter	$[m^2/N]$
$\tilde{\Delta}\beta$	Non-ideal compressibility parameter	$[m^2/N]$
$\Delta\beta_{Siani}$	Non-ideal compressibility parameter in the model of Siani	$[m^2/N]$
γ	Adiabatic Constant	[-]
δ	Perturbation in parameter p	various
δ	Thickness, distance	$[m]$
Δ	Difference	various
η	Ratio between original and inhibited reactivity ratio	[-]
η	Dynamic shear viscosity	$[Pa\ s]$
λ	Eigenvalue	[-]
λ	Wavelength	$[m]$
$\mathcal{L}$	Lie-derivative	[-]
μ	Monomer consumption	$[mol/s]$
ν	Monomer concentration ratio	[-]
ω	Angular velocity	$[Hz]$
ω	Vector containing model error or model noise	mixed
ρ	Density	$[g/l]$
σ	Thermal conductivity	$[W/m/K]$
ϕ	Volume fraction	[-]
ϕ_{cr}	Critical volume fraction for glass transition	[-]
ϕ_{MG}	Volume fraction at which $\Delta\beta_{Siani} = 0$	[-]
φ	Approximate solution of the distribution variance of N_n	[-]
φ	Vector of measurement noise	mixed
Φ_{Pol}^p	Polymer fraction of the particle volume	[-]

Subscripts

<i>bb</i>	Backbiting
<i>cr</i>	critical
<i>d</i>	Discrete
<i>end</i>	at final duration
<i>CTA</i>	Chain transfer agent
<i>e</i>	effective
<i>E</i>	Emulsifier
<i>Env</i>	Environment
<i>Feed</i>	Feed stream
<i>i</i>	Component <i>i</i> , monomer <i>i</i>
<i>in</i>	ingoing stream
<i>I</i>	Initiator
<i>Inh</i>	Inhibited
<i>J</i>	Jacket
<i>k</i>	Discrete Time Point
<i>l</i>	lower
<i>m</i>	Monomer feed
<i>meas</i>	measurement
<i>M</i>	Monomer
<i>Mi</i>	Monomer <i>i</i>
<i>LB</i>	Lower parameter bound
<i>n</i>	normalized
<i>opt</i>	optimal
<i>out</i>	Outgoing stream
<i>Pol</i>	Polymer
<i>Poli</i>	Polymer <i>i</i>
<i>max</i>	Maximum
<i>min</i>	Minimum
<i>R</i>	Reactor
<i>sat</i>	saturation
<i>t</i>	temperature gradient
<i>tot</i>	total
<i>u</i>	upper
<i>UB</i>	Upper parameter bound
<i>W</i>	Water
<i>x</i>	at distance <i>x</i>
0	at start duration, at start location, for reference component

Superscripts

<i>ad</i>	adiabatic
<i>d</i>	Droplet phase

NOMENCLATURE

h	Hairy layer
max	Maximum
p	Particle phase
opt	optimization vector
$\dot{Q}$	heat
R	Reactor
sat	saturation
set	Setpoint
w	Water phase