Optimal Grade Transitions in a Gas-phase Polymerization Fluidized Bed Reactor

Yajun Wang, Lorenz T. Biegler

Center of Advanced Process Decision-making

Department of Chemical Engineering

Carnegie Mellon University

Rita Majewski, George Ostace

Braskem America

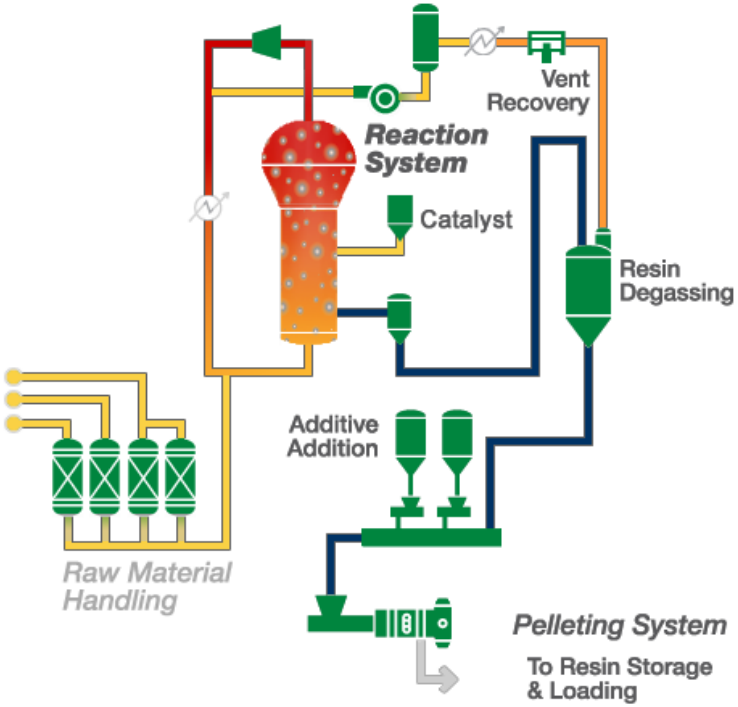
Enterprise Wide Optimization Meeting, September 30, 2015

Introduction

Motivation

Polymer products change frequently.

- The transition usually takes *hours*.
- *Tons of off-specification polymers* are generated.

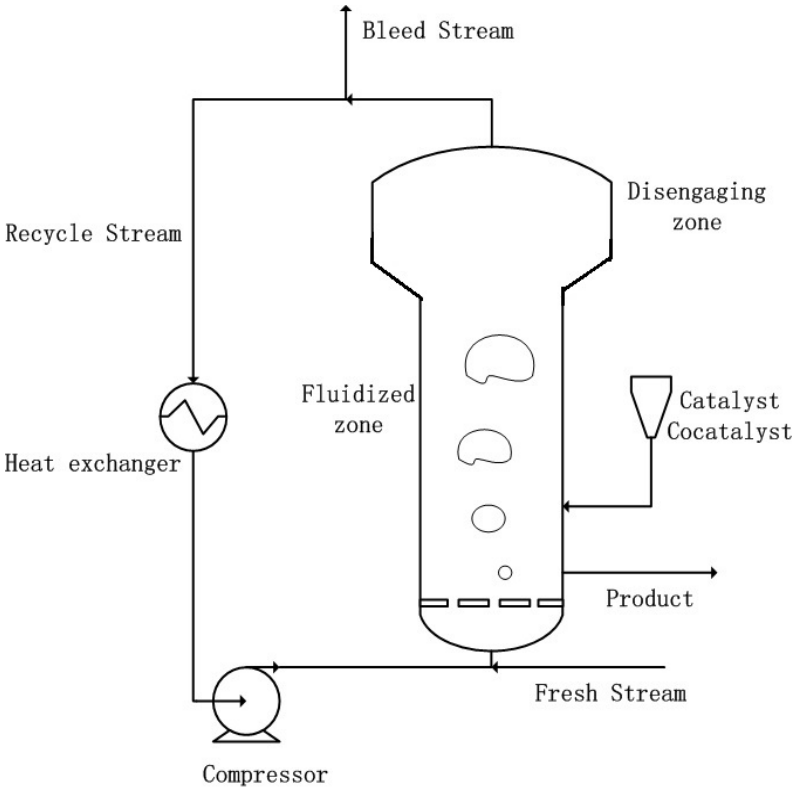


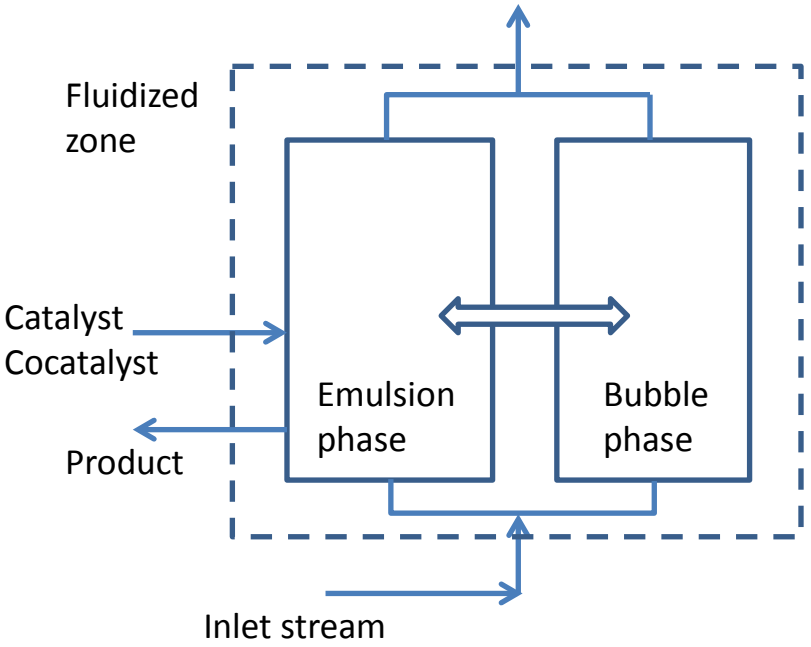
Objective

- The objective is to reduce the transition time and off-specification products, while guaranteeing the product property requirements.
- Dynamic optimization is carried out to determine optimal operation sequences in grade transitions.

Figure source: http://www.univation.com/unipol.animation.html

Fluidized bed reactor (FBR)





Gas feeds:

- C-3 inlet flow
- C-2 inlet flow
- H_2 inlet flow
- N_2 inlet flow

Solid feeds:

- Catalysts
- Cocatalysts

Two-phase model

- Emulsion Phase
  - Solids and gases
  - Minimum fluidization
  - Polymerization reactions
- Bubble Phase
  - Gases only

Polymerization reactions

Reaction step	Reactant	Reaction	Rate constant
Site activation	Hydrogen	$C_P + H_2 \rightarrow P_0$	k_{AH}
	Cocatalyst	$C_P + A \rightarrow P_0 + B$	k_{AA}
Chain initiation	Monomer i	$P_0 + M_i \rightarrow P_{1,i}$	k_{Ii}
Chain propagation	Monomer j	$P_{n,i} + M_j \rightarrow P_{n+1,j}$	k_{Pj}
Chain transfer	Hydrogen	$P_{n,i} + H_2 \rightarrow P_0 + D_{n,i}$	k_{TH}
	Monomer j	$P_{n,i} + M_j \rightarrow P_{1,j} + D_{n,i}$	k_{TMj}
	Spontaneous	$P_{n,i} \rightarrow P_0 + D_{n,i}$	k_{TS}
Site deactivation	Spontaneous	$P_{n,i} \rightarrow C_d + D_{n,i}$ $P_0 \rightarrow C_d$	k_{DS}

C_P: potential site P_0: activated site
C_d: dead site A: cocatlyst
M_i: monomer i, $i \in \{C_3H_6, C_2H_4\}$
$P_{n,i}$: live polymer with chain length n and end group M_i
$D_{n,i}$: dead polymer with chain length n and end group M_i

Moment model

$$\text{Live polymer moments:} \quad \mu_k = \sum_{n=1}^{\infty} n^k [P_n]$$

$$\text{Bulk polymer moments:} \quad \lambda_k = \sum_{n=1}^{\infty} n^k ([P_n] + [D_n])$$

- First three moments are sufficient to describe some properties, like MFI.
- Instead of listing rate equations of all polymer chains, only equations for leading moments are required.

Moments	Reaction Rate
Zero order	$R_{\mu_0} = \sum_{i=1}^{NM} (k_{Ii}[P_0][M_i]) - ((k_{TH} + k_{DH})[H_2] + (k_{TS} + k_{DS}))\mu_0$
	$R_{\lambda_0} = \sum_{i=1}^{NM} k_{Ii}[P_0][M_i]$
First order	$R_{\mu_1} = \sum_{i=1}^{NM} (k_{Ii}[P_0][M_i] + k_{Pi}[M_i]\mu_0 + k_{TMi}[M_i](\mu_0 - \mu_1)) - ((k_{TH} + k_{DH})[H_2] + (k_{TS} + k_{DS}))\mu_1$
	$R_{\lambda_1} = \sum_{i=1}^{NM} (k_{Ii}[P_0][M_i] + k_{Pi}[M_i]\mu_0 + k_{TMi}[M_i]\mu_0)$
Second order	$R_{\mu_2} = \sum_{i=1}^{NM} (k_{Ii}[P_0][M_i] + 2k_{Pi}[M_i]\mu_1 + k_{TMi}[M_i](\mu_0 - \mu_2)) - ((k_{TH} + k_{DH})[H_2] + (k_{TS} + k_{DS}))\mu_2$
	$R_{\lambda_2} = \sum_{i=1}^{NM} (k_{Ii}[P_0][M_i] + 2k_{Pi}[M_i]\mu_1 + k_{TMi}[M_i]\mu_0)$

Mass and energy balance in FBR

- Emulsion Phase

$$\frac{d[Y_i]_e}{dt} = \frac{U_e}{H}([Y_i]_{in} - [Y_i]_e) + \frac{(1-\delta)K_{be}}{\delta\epsilon_{mf}}([Y_i]_b - [Y_i]_e) + \frac{1-\epsilon_{mf}}{\epsilon_{mf}}R_i - \frac{[Y_i]_e}{H}\frac{dH}{dt}$$

$$\frac{d[S_j]}{dt} = \frac{Q_{in,j}}{V_e(1-\epsilon_{mf})}[S_j]_{in} - \frac{Q_{out}}{V_e}[S_j] + R_j - \frac{[S_j]}{H}\frac{dH}{dt}$$

$$\frac{dT_e}{dt} = \frac{1}{\sum_i V_e\epsilon_{mf}[Y_i]_e Cp_i + V_e(1-\epsilon_{mf})\rho_{pol}Cp_{pol}}(U_eA_e\epsilon_{mf}\sum_i[Y_i]_{in}\int_{T_e}^{T_{in}} Cp_i dT$$
$$+V_e(1-\epsilon_{mf})R_{pol}\Delta H_{pol} + V_bH_{be}(T_b - T_e) + V_bK_{be}\sum_i([Y_i]_b - [Y_i]_e)\int_{T_e}^{T_b} Cp_i dT)$$

- Bubble Phase

$$\frac{d[Y_i]_b}{dt} = \frac{U_b}{H}([Y_i]_{in} - [Y_i]_b) - K_{be}([Y_i]_b - [Y_i]_e) - \frac{[Y_i]_b}{H}\frac{dH}{dt}$$

$$\frac{dT_b}{dt} = \frac{1}{\sum_i V_b[Y_i]_b Cp_i}(U_bA_b\sum_i[Y_i]_{in}\int_{T_b}^{T_{in}} Cp_i dT - V_bH_{be}(T_b - T_e))$$

Property predictions

- Empirical correlations for MFI[1]

$$MFI = a \times (\overline{Mw})^b$$

where the weight average molecular weight, $\overline{Mw} = W\lambda_2 / \lambda_1$
(W is the average molecular weight of one unit in polymers.)

- ODE equations for cumulative composition Φ_{C3H6} [2]

$$\frac{d(\mathrm{M}_{pol}\,\Phi_{C_3H_6})}{dt} = -V_e(1-\varepsilon_{mf})\phi_{C_3H_6}\sum_i R_i W_i - Q_{out}(1-\varepsilon_{mf})(1-\delta)\Phi_{C_3H_6}$$

where Mpol is the mass in the reactor,
Wi is the molecular weight of monomer i,
$\phi_{C_3H_6}$ is the instantaneous composition of propylene.

[1] Ahmmed S Ibrehem, Mohamed A Hussain, and Nayef M Ghasem. Modified mathematical model for gas phase olefin polymerization in fluidized-bed catalytic reactor. Chemical Engineering Journal, 149(1):353–362, 2009.
[2] C Chatzidoukas, JD Perkins, EN Pistikopoulos, and C Kiparissides. Optimal grade transition and selection of closed loop controllers in a gas-phase olefin polymerization fluidized bed reactor. Chemical Engineering Science, 58(16):3643–3658, 2003.

Polymer grades

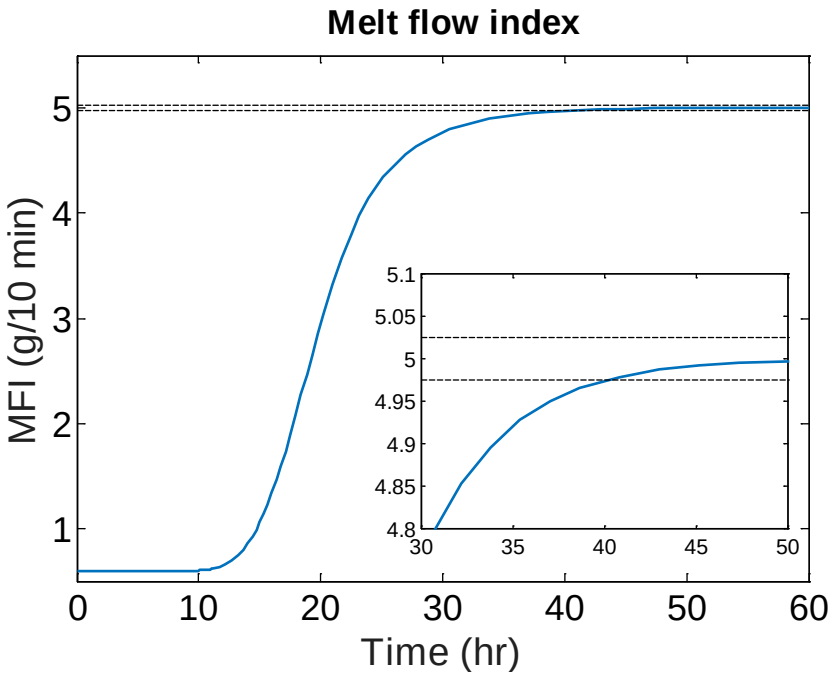
Grade properties and operation conditions for two different grades.

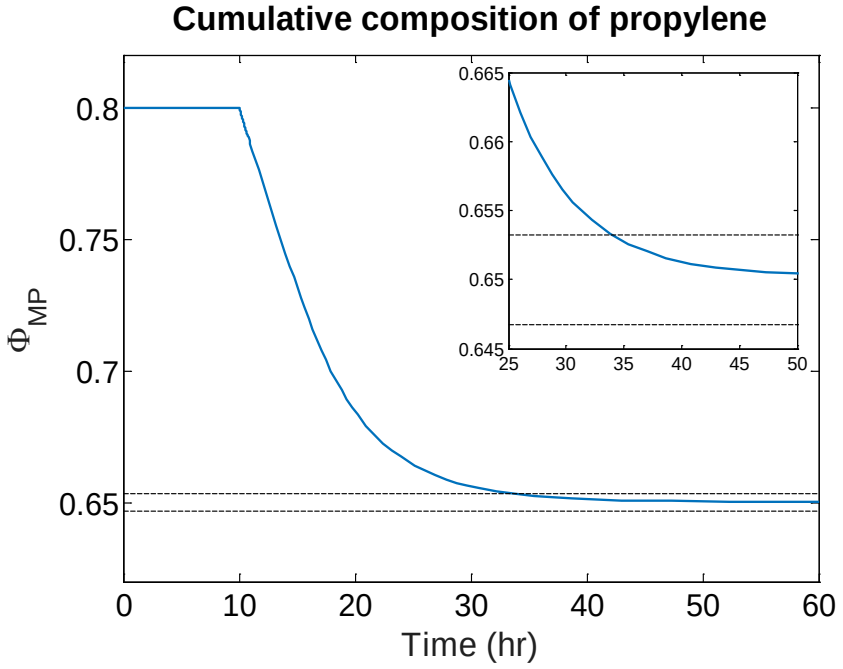
		Grade A	Grade B
End-use properties	MFI $(g/10min)$	0.6	5
	$\Phi_{C_3H_6}$	0.8	0.65
	Production (ton/hr)	17	17
Manipulated variables	C-3 inlet flowrate (m^3/s)	1.64	1.35
	C-2 inlet flowrate (m^3/s)	1.37	2.38
	H_2 inlet flowrate (m^3/s)	6.60×10^{-2}	0.23
	N_2 inlet flowrate (m^3/s)	0.20	0.51
	Catalyst inlet flowrate (m^3/s)	2.22×10^{-4}	3.79×10^{-4}
	Cocatlyst inlet flowrate (m^3/s)	2.67×10^{-4}	3.87×10^{-4}
	Product outlet flowrate (m^3/s)	1.04×10^{-2}	1.07×10^{-2}
	Inlet temperature (K)	346.7	344.0

The transition from grade A to grade B is studied.

Step response

- The system initially produces polymers in grade A
- At 10 hours, the operation conditions change to grade B.





- The transition ends when the properties reach and stay within a small region around the desired properties.
- The transition time for step change is around **27 hours**.

Optimization formulation

$$\min_{z,u} \quad \int_{t_0}^{t_f} \alpha||Q - Q^\star||^2 + \beta||u - u^\star||^2 dt$$

s.t.

$$\frac{dz(t)}{dt} = F(z(t), y(t), u(t), t)$$

$$0 = G(z(t), y(t), u(t), t)$$

$$z^L \leq z(t) \leq z^U$$

$$y^L \leq y(t) \leq y^U$$

$$u^L \leq u(t) \leq u^U$$

Mass/energy balance
Volume change
Cumulative composition

Hydrodynamics
Pressure
MFI

Q: properties (MFI, Φ_{C3H6})

z: state variables
(concentrations, moments, temperature)

u: manipulated variables
(feed flowrates, feed temperature)

y: algebraic variables (pressure)

The dynamic optimization problem is solved by a simultaneous approach

Finite element number

Number of Finite elements	20	40	80	300
Number of equations	1.62×10^3	3.24×10^3	6.48×10^3	2.43×10^4
Solve time (sec)	71.67	465.48	1726.5	5572.8
Iterations	285	691	1236	948
Scaled objective values	8.86×10^{-2}	8.80×10^{-2}	8.69×10^{-2}	8.68×10^{-2}
Transition time (hr)	14.1	13.0	12.3	12.3

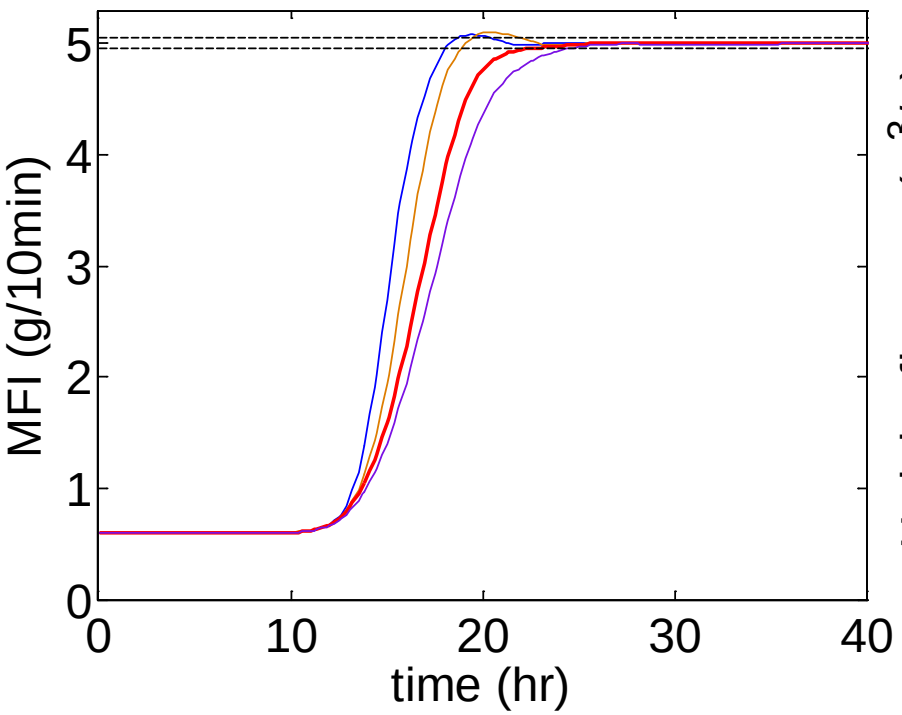
Fewer finite elements → faster to solve; larger objective value and longer transition time
More finite elements → slower to solve; better objective values and shorter transition time

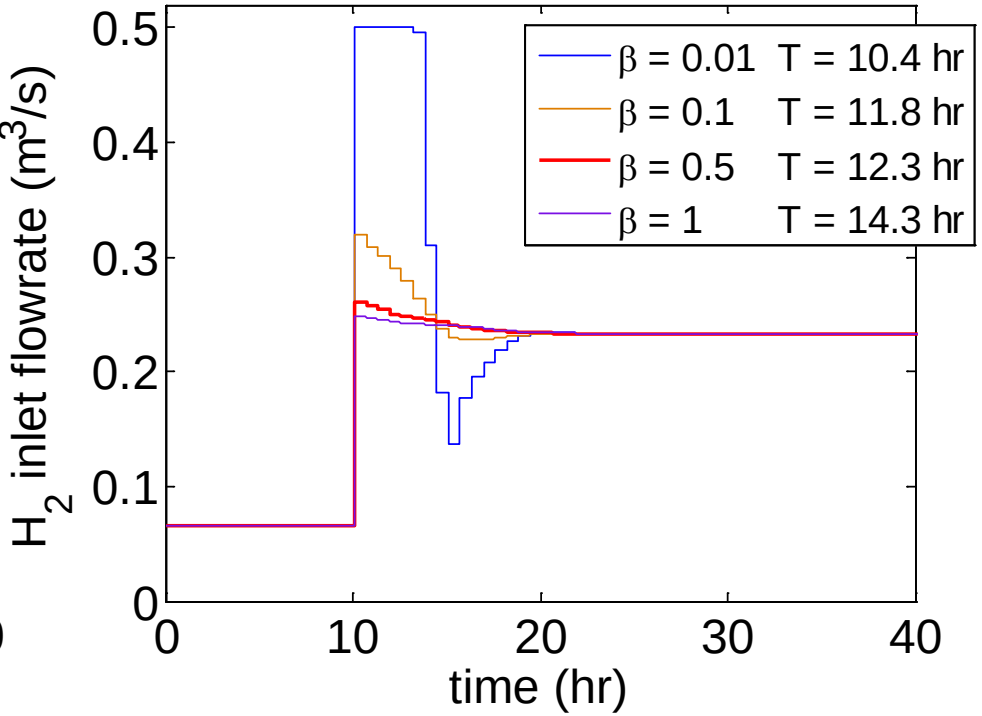
✓ **80 finite elements**, considering the optimization results and computational time.

Weight factors

$$\min_{z,u} \quad \int_{t_0}^{t_f} \; ||\frac{Q}{Q^\star} - 1||^2 + \beta||\frac{u}{u^\star} - 1||^2 dt$$

The objective function is scaled. α is fixed to 1 and only β varies.





Small β ⟶ fast transition; severe offset and oscillations

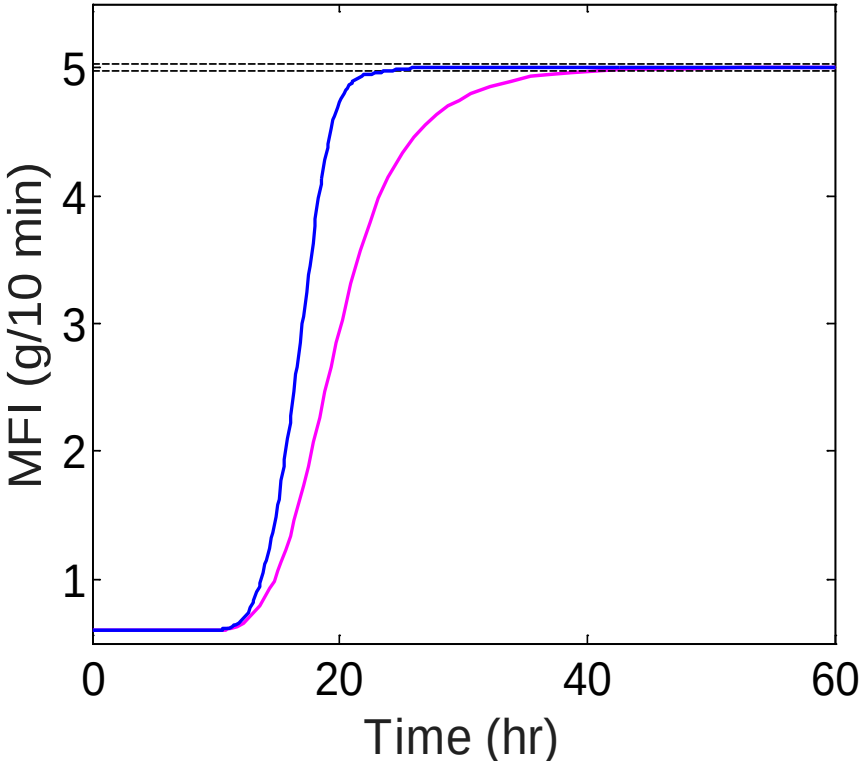
Large β ⟶ slow transition; smooth responses

✓ **β=0.5**, considering transition time and smoothness.

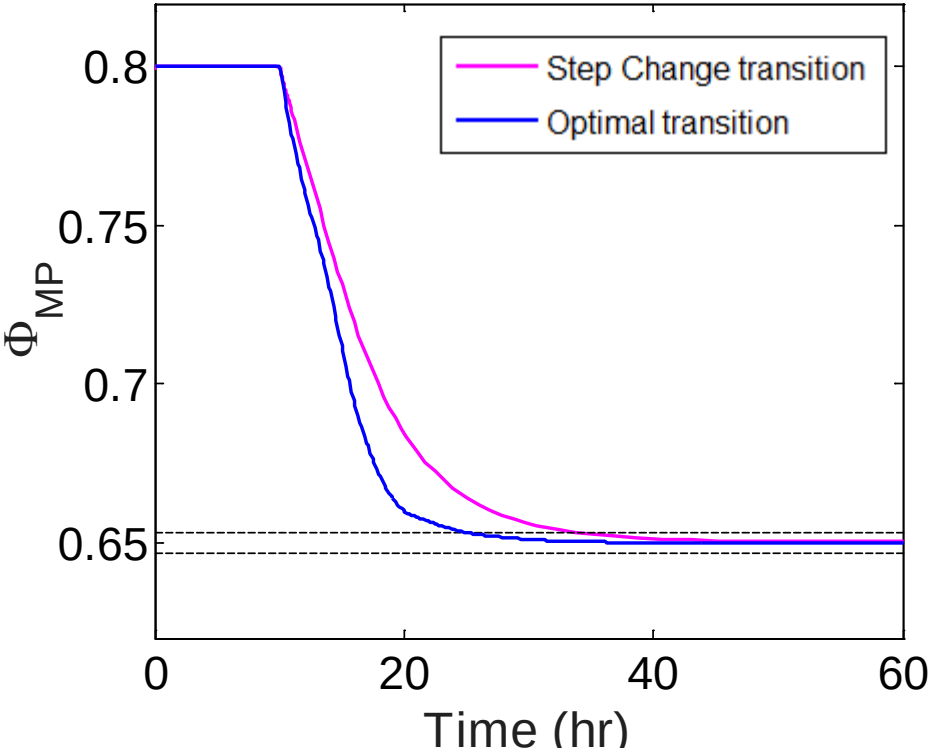
Optimization results --- properties

Run optimization problem with **80 finite elements** and **weight factor β = 0.5**

Melt flow index



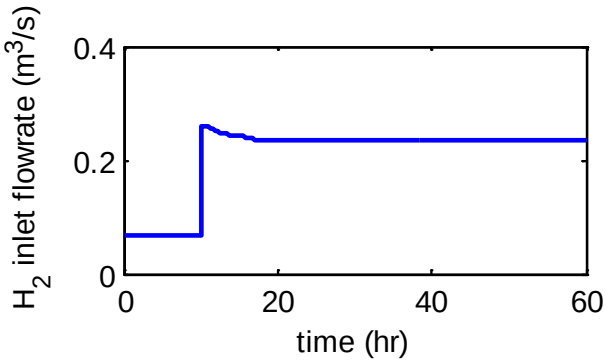
Cumulative composition of propylene

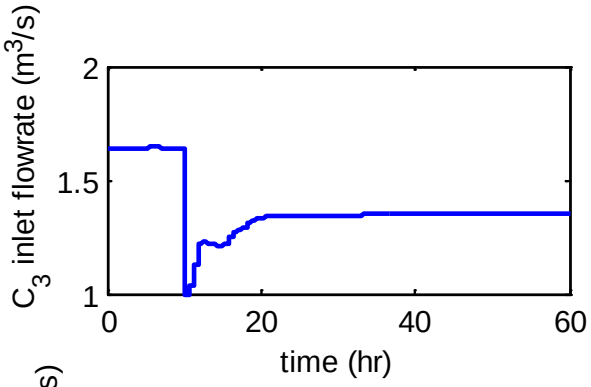


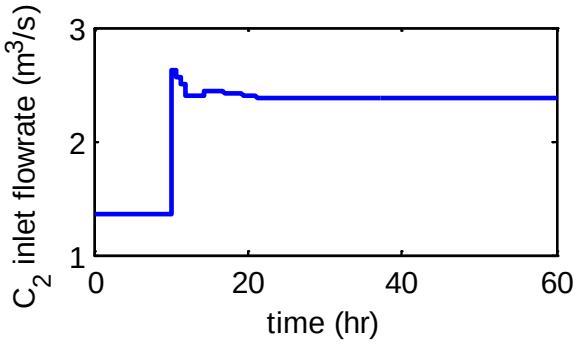
The transition time is cut by **54.4%**. (reduced from 27 hrs to 12.3 hrs).
The production of off-grade polymers is reduced by **54.0%.**

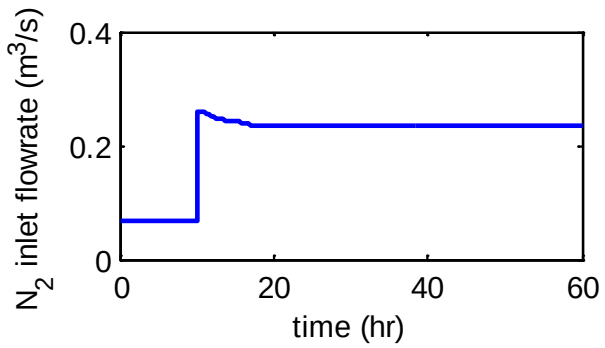
Optimization results --- manipulated variables

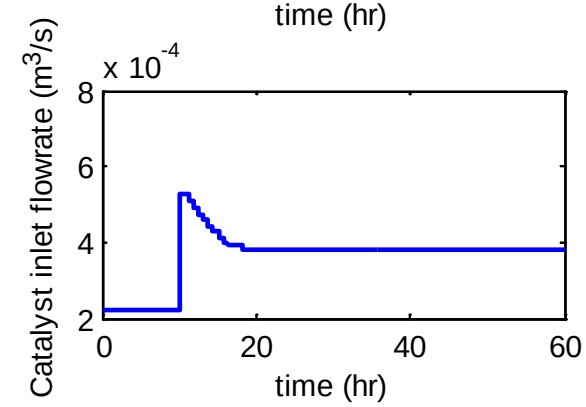
Run optimization problem with **80 finite elements** and **weight factor β = 0.5**

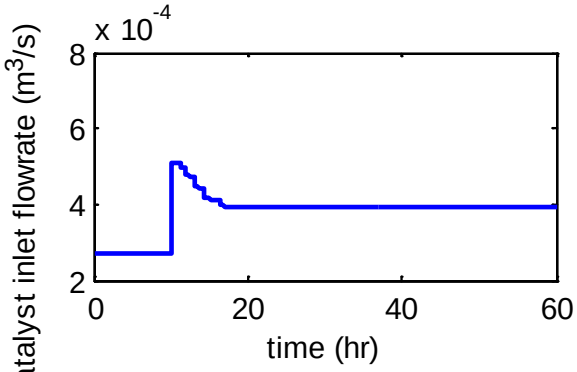


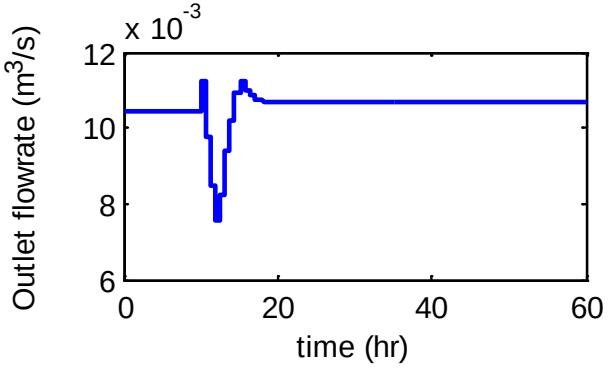


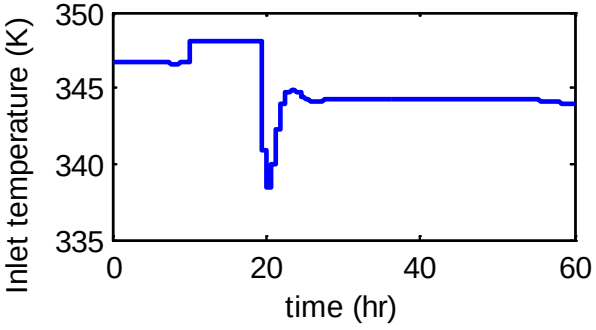












Conclusions and future work

- Developed a dynamic **model** of propylene/ethylene copolymerization in the fluidized bed reactor.
- Simulated the **grade transition** behaviors.
- Solved the **dynamic optimization** problem by a simultaneous method. The transition time is cut down by more than half.
- Considered the effects of **finite element number and weight factors**.

- Extend the model for multiple site catalysts with site transformation reactions.
- Implement VLE model to prevent gas phase condensation. Surrogate models may be considered.
- Modify the objective functions to take off-spec products into account directly.