Simulation of unsteady-state modes of operation in slurry phase HDPE production

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Introduction

- Polyolefins
  - Bulk commodity chemical
  - High density polyethylene
  - Slurry phase continuous reactor
  - Ziegler-Natta catalyst

Introduction

- Grade transitions
  - Unsteady state operation
  - Off-spec material
  - Rules of thumb and empirical correlations

Introduction

- Unsteady-state reactor model
  - Fundamental kinetic model
  - Hydrodynamics and mixing
  - Computationally efficient mathematical structure

Population Balance Model

- Common approach to dynamic reactor models
- Hulbert & Katz (1964):

$$\frac{\delta\Psi}{\delta t}+\sum_i \frac{\delta}{\delta\alpha_i}\left(\frac{\delta\alpha_i}{\delta t}\Psi\right)=B-D$$

- Predict moments

$$\overline{\alpha_i}=\int_{\underline{\alpha}}\alpha_i\underline{\underline{\Psi}}(\underline{\alpha})d\underline{\alpha}$$

Population Balance Model

- Accurately simulate polymerisation reaction systems
    - Kiparissides et al
- Computationally intensive
    - Multidimensional PDEs
    - Solution times 250 – 25 000 s (Alexopoulos et al, 2009)

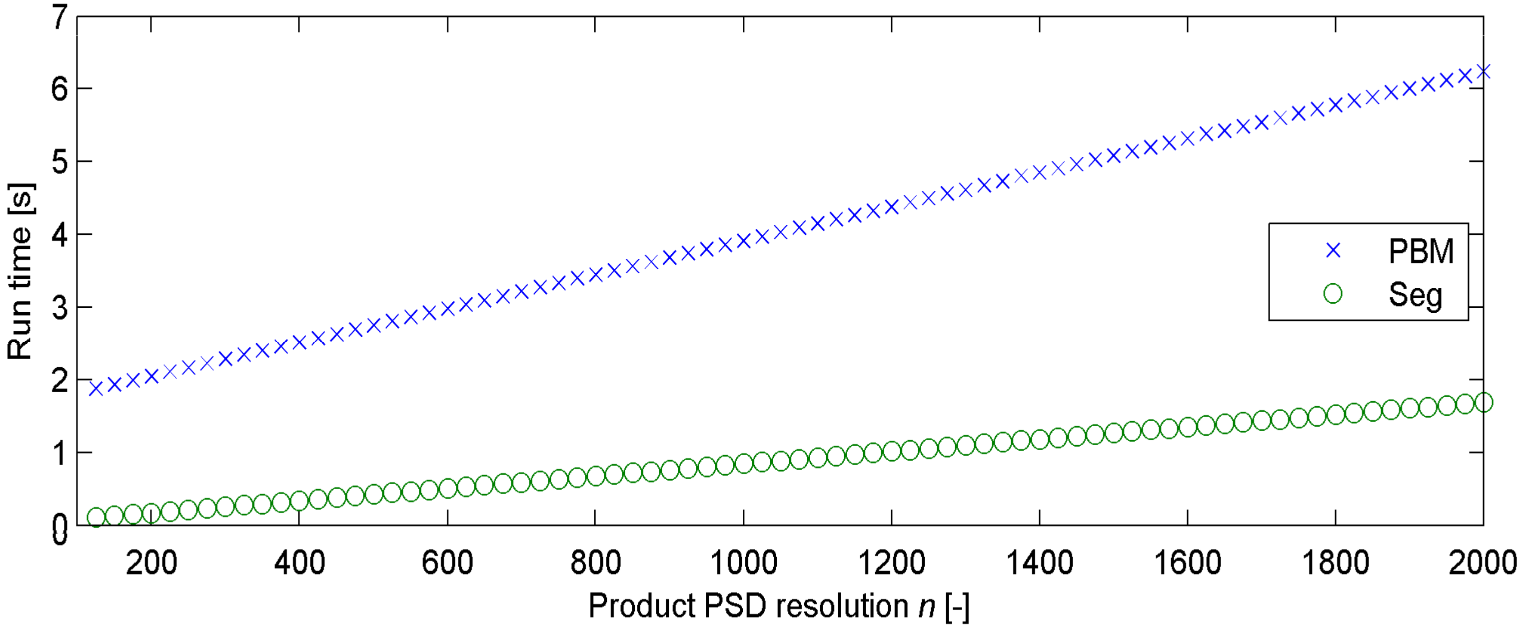
Segregation approach

- Efficient alternative to PBM (Rawatlal, 2009, McCoy and Rawatlal, 2011b)
- Reformulation in terms of:
  - Feed conditions
  - Residence time distribution

$$\overline{\alpha_i} = \iint \alpha_i\left(\alpha_{i,0}, \theta\right) \Psi_0\left(\alpha_{i,0}\right) I(\theta)\, d\alpha_{i,0}\, d\theta$$

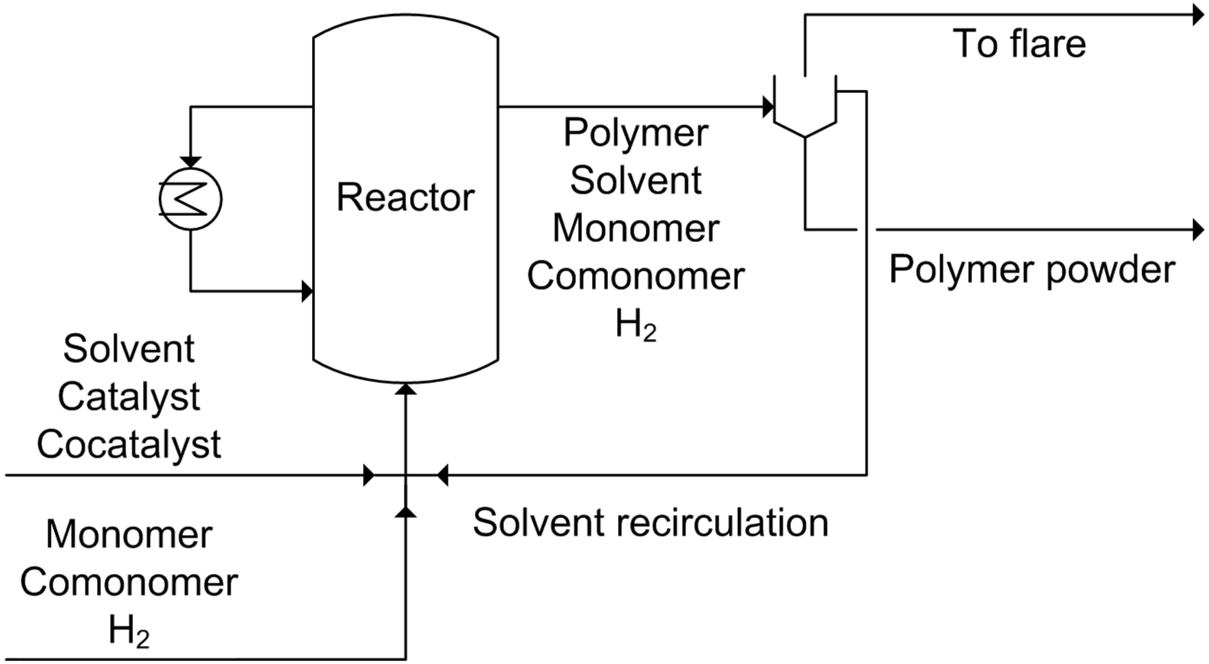
Segregation approach

- Solution time of PSD models (McCoy & Rawatlal, 2011b)



Model development

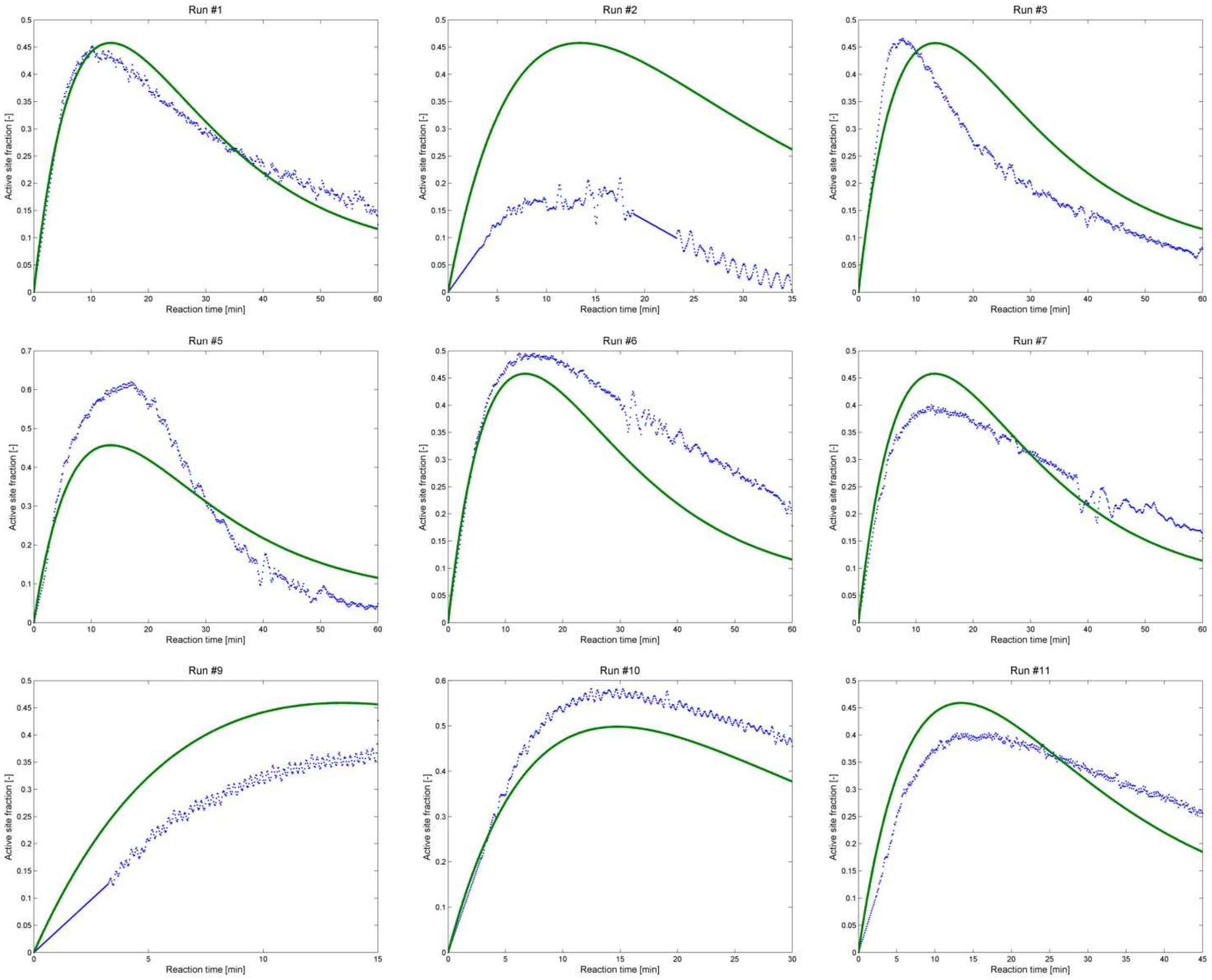
- Well-mixed slurry reactor
- Ethylene-1-butene copolymer
- Ziegler-Natta catalyst



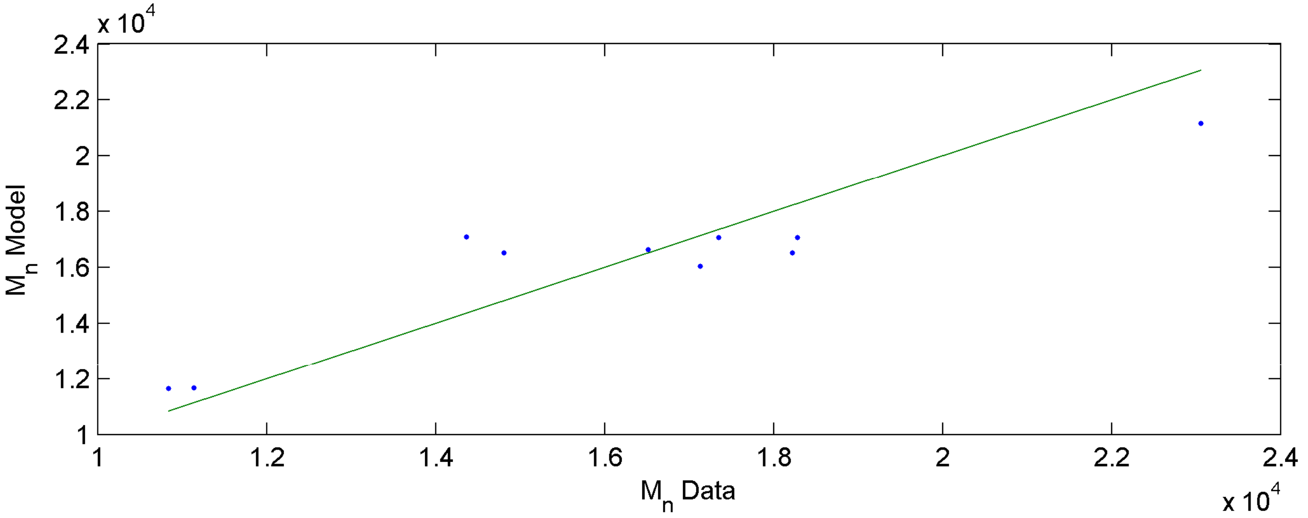
Kinetic development

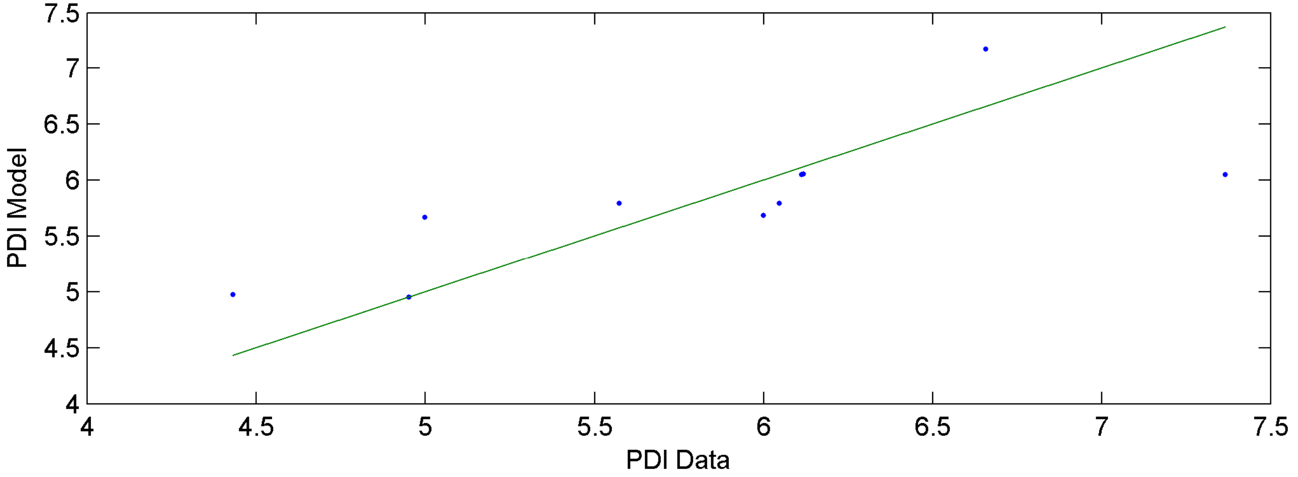
	Reaction	Rate constant
Catalytic reactions		
Site transformation		
Spontaneous	$P_*^q \rightarrow P_0^r + D_n^q$	$k_{st,sp}^{q,r}$
Aluminium Alkyl (*A*)	$P_*^q + \alpha_A A \rightarrow P_0^r + D_n^q$	$k_{st,A}^{q,r}$
Hydrogen (H_2)	$P_*^q + \alpha_{H_2} H_2 \rightarrow P_0^r + D_n^q$	$k_{st,H_2}^{q,r}$
Polymeric reactions		
Propagation		
Initiation	$P_0^q + M_i \rightarrow P_{1,i}^q$	$k_{0,i}^q$
Propagation	$P_{n,i}^q + M_j \rightarrow P_{n+1,j}^q$	$k_{p,ij}^q$
Termination		
Spontaneous	$P_{n,i}^q \rightarrow P_0^q + D_{n,i}^q$	$k_{t,sp}^q$
Aluminium Alkyl (*A*)	$P_{n,i}^q + A \rightarrow P_0^q + D_{n,i}^q$	$k_{t,A}^q$
Monomer (M_i)	$P_{n,i}^q + M_i \rightarrow P_{1,i}^q + D_{n,i}^q$	k_{t,M_i}^q
Hydrogen (H_2)	$P_{n,i}^q + H_2 \rightarrow P_0^q + D_{n,i}^q$	k_{t,H_2}^q

Kinetic development



Kinetic development





Kinetic development

- Kinetic parameters
  - From experimental data (unpublished)

k_p	12.98			[L.min^{-1}.g-cat^{-1}]	
$i =$	**sp**	**A**	**M_1**	**M_2**	**H_2**
$[k_{st}]$	[min^{-1}]	[min^{-1}.{mol-TEA.L^{-1}}$^{-1}$]	-	-	[min^{-1}.{mol-H_2.L^{-1}}$^{-0.5}$]
$k_{st,i}^{4+,3+}$	9.00E-02	1.47E+00	-	-	2.73E-03
$k_{st,i}^{3+,2+}$	2.05E-10	8.73E-01	-	-	3.27E-01
$k_{st,i}^{2+,3+}$	4.22E-03	1.27E-04	-	-	2.08E-04
$[k_t]$	[min^{-1}]	[min^{-1}.{mol-TEA.m^{-3}}$^{-1}$]	[min^{-1}.{mol-M_1.m^{-3}}$^{-1}$]	[min^{-1}.{mol-M_2.m^{-3}}$^{-1}$]	[min^{-1}.{mol-H_2.m^{-3}}$^{-1}$]
k_t^i	0.0586	0.0134	0.0057	0.0014	0.0216

Model development

- Component balances

$$\frac{dN}{dt} = F_0 - \frac{N}{\tau_{out}} - n_{Ti} m_{cat}(t) \overline{r_N}\left(N, \underline{P_*}\right)$$

Flow in Flow out Consumption

- Active site balances

$$\frac{\delta P_*^{4+}}{\delta t} + \frac{\delta P_*^{4+}}{\delta \theta} = -\beta_{st}^{4+,3+} P_*^{4+}$$

$$\frac{\delta P_*^{3+}}{\delta t} + \frac{\delta P_*^{3+}}{\delta \theta} = \beta_{st}^{4+,3+} P_*^{4+} - \beta_{st}^{3+,2+} P_*^{3+} + \beta_{st}^{2+,3+} P_*^{2+}$$

$$\frac{\delta P_*^{2+}}{\delta t} + \frac{\delta P_*^{2+}}{\delta \theta} = \beta_{st}^{3+,2+} P_*^{3+} - \beta_{st}^{2+,3+} P_*^{2+}$$

$$P_*^{4+}(0) = 1; \; P_*^{3+}(0) = P_*^{2+}(0) = 0$$

Model development

- Monomer consumption

$$r_{M_i} = \frac{dM_i}{dt} = [M_i]\left(\sum_j \lambda_{0,j}\left(k_{p,ji} + k_{t,j}^{M_i}\right)\right)$$

- Hydrogen/co-catalyst consumption

$$r_X = \frac{dX}{dt} = [X]\left(\sum_i \lambda_{0,i} k_{t,i}^{X} + \sum_q \alpha^{q,r} k_{st,X}^{q,r} P_*^q\right)$$

- Age contributions

$$\overline{r_N} = \int_0^\infty r_N\left(N, \underline{P_*}\right) I(t,\theta)\, d\theta$$

Model development

- Polymer properties
  - Pseudo-sites (Rawatlal, 2004, McCoy & Rawatlal, 2011a)
  - Live moments

$$\lambda_0 = P_* \sum_m f^m \sum_i \xi_i^m$$

$$\lambda_1 = P_* \sum_m f^m \sum_i \xi_i^m \frac{1}{1-\gamma^m}$$

$$\lambda_2 = P_* \sum_m f^m \sum_i \xi_i^m \frac{1+\gamma^m}{\left(1-\gamma^m\right)^2}$$

Model development

- Peng-Robinson EoS
  - Each step of ODE solver
- Method of lines (Schiesser, 1991)
- Mean particle size
  - Extension of models presented in previous work (McCoy & Rawatlal, 2011b)

Model vs Industrial data

- Steady state plant data

Grade	**1**	**2**	**3**	**4**
H_2:C_2 ratio	**1.6**	**0.89**	**1.5**	**0.47**
Catalyst efficiency (ton C_2/ kg cat)	2.8	6.4	3.8	8.8
MFI (5/190)	21.8	10.5	28.9	1.59
TEA analysis (mmol/l)	0.695	1.25	0.665	0.800

- Model results

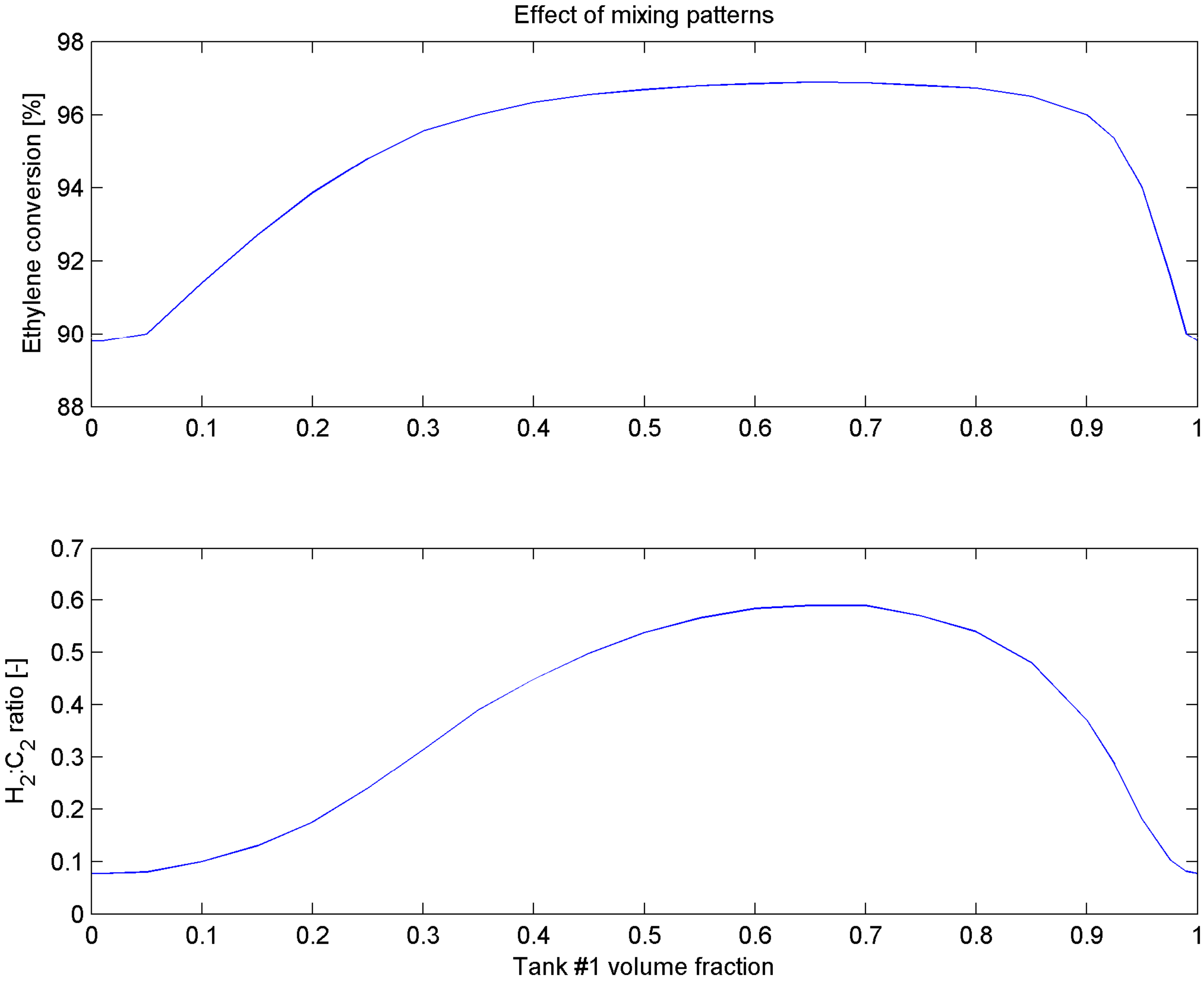
Grade	**1**	**2**	**3**	**4**
H_2:C_2 ratio	**0.077**	**0.027**	**0.056**	**0.015**
Catalyst efficiency (ton C_2/ kg cat)	3.02	6.25	4.02	8.3
MFI (5/190)	0.25	0.023	0.11	5.40E-03
TEA analysis (mmol/l)	0.698	1.12	0.71	0.78
PDI	10.1	14.9	11.2	21.5
M_n	2.07E+04	2.85E+04	2.40E+04	3.03E+04
C_2 conversion (%)	**89.8**	**81.8**	**87.5**	**80.1**

Model vs Industrial data

- Low conversion
- Kinetic parameters
  - Experimental campaign

- Mixing patterns non-ideal?
- Tanks-in-series
  - Two tanks
  - Unequal volumes

Mixing pattern

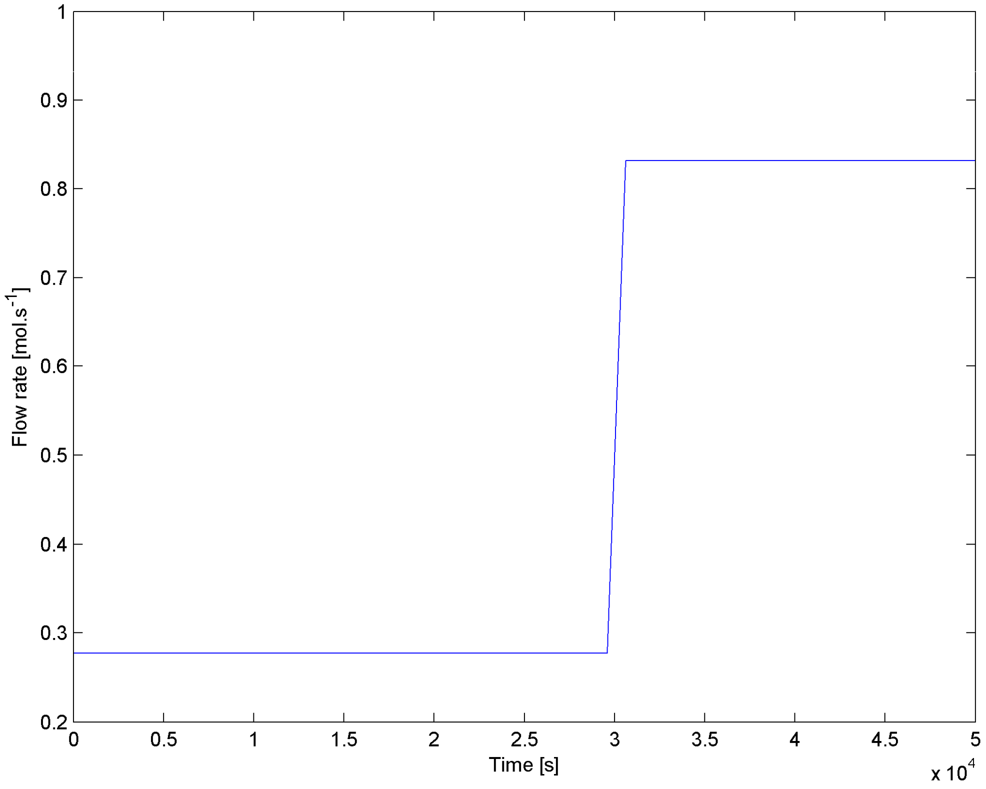


Mixing pattern

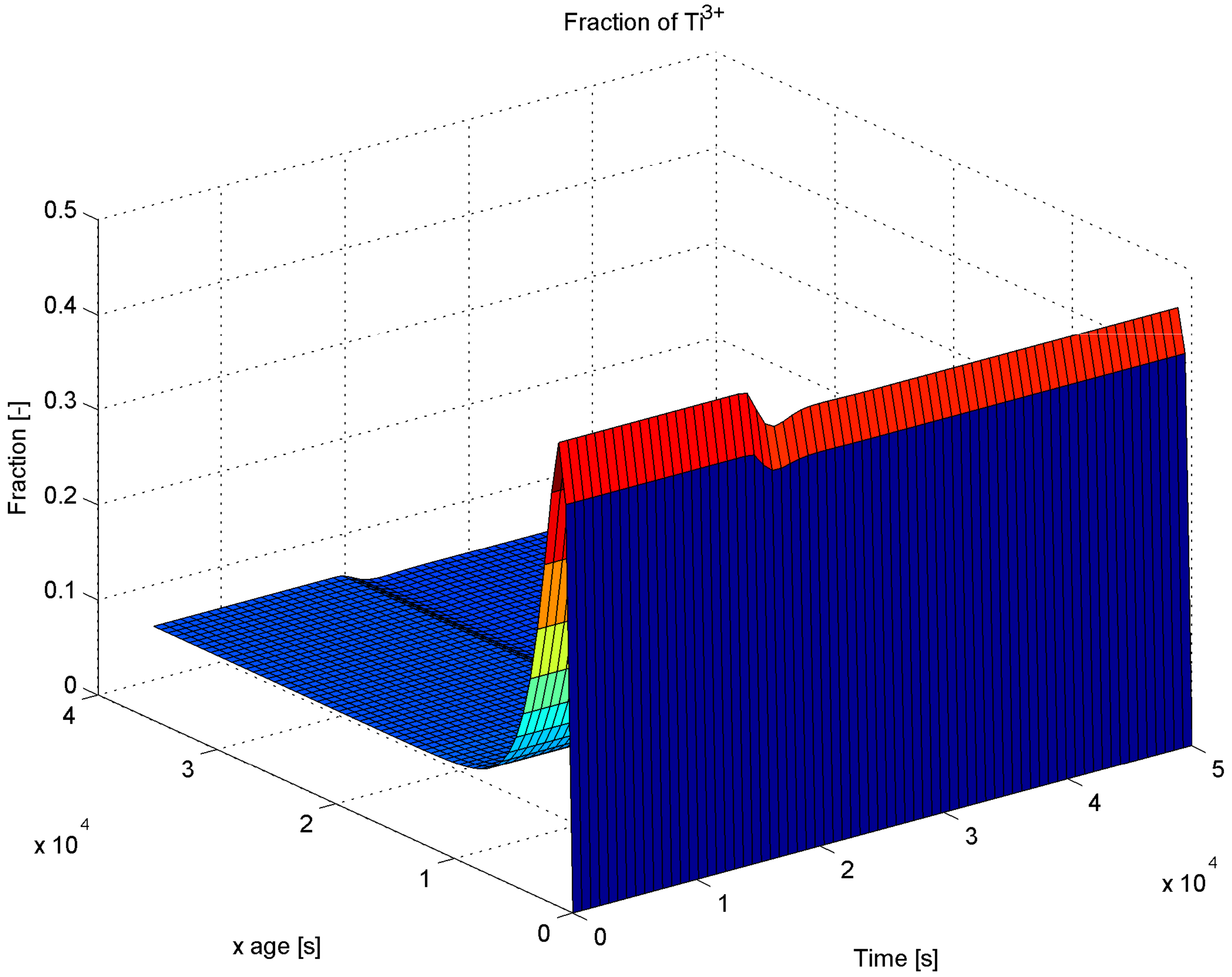
- Perfect mixing assumption incorrect
- Significant effect on model
- Further investigation required
  - Internals of reactor
  - More complex mixing patterns / RTD functions

Unsteady state simulation

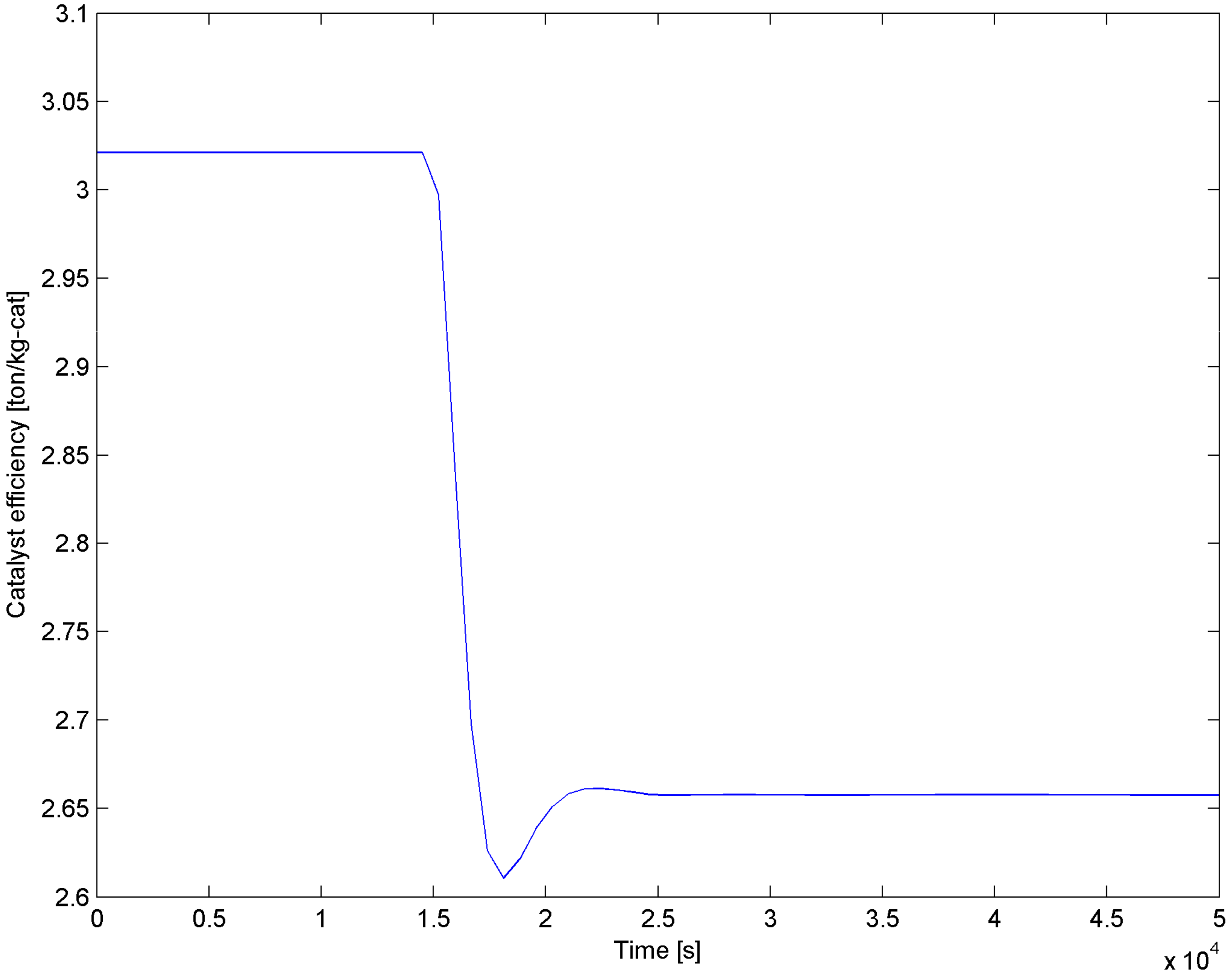
- Illustrate computational efficiency
- Step change in hydrogen feed



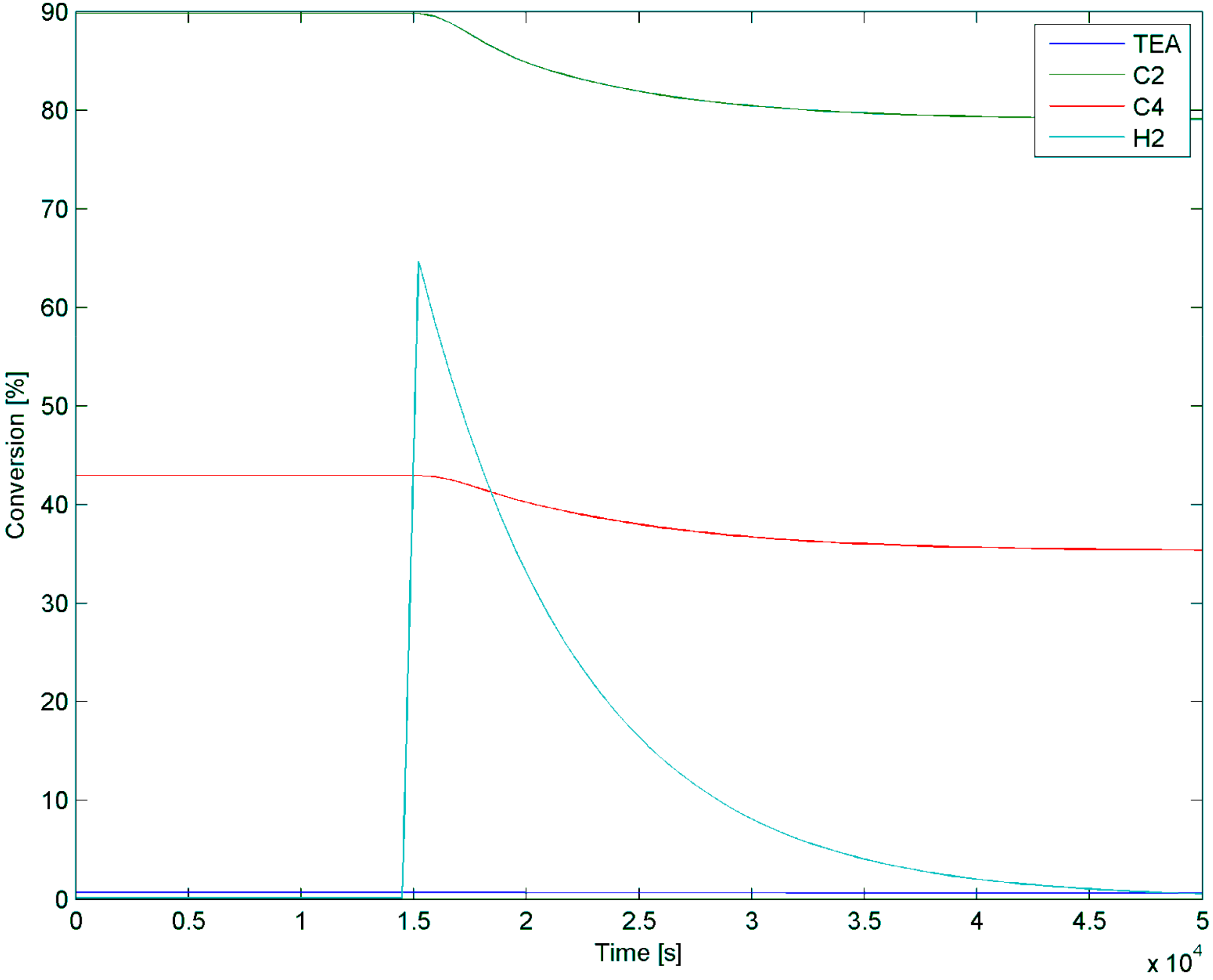
Unsteady state simulation



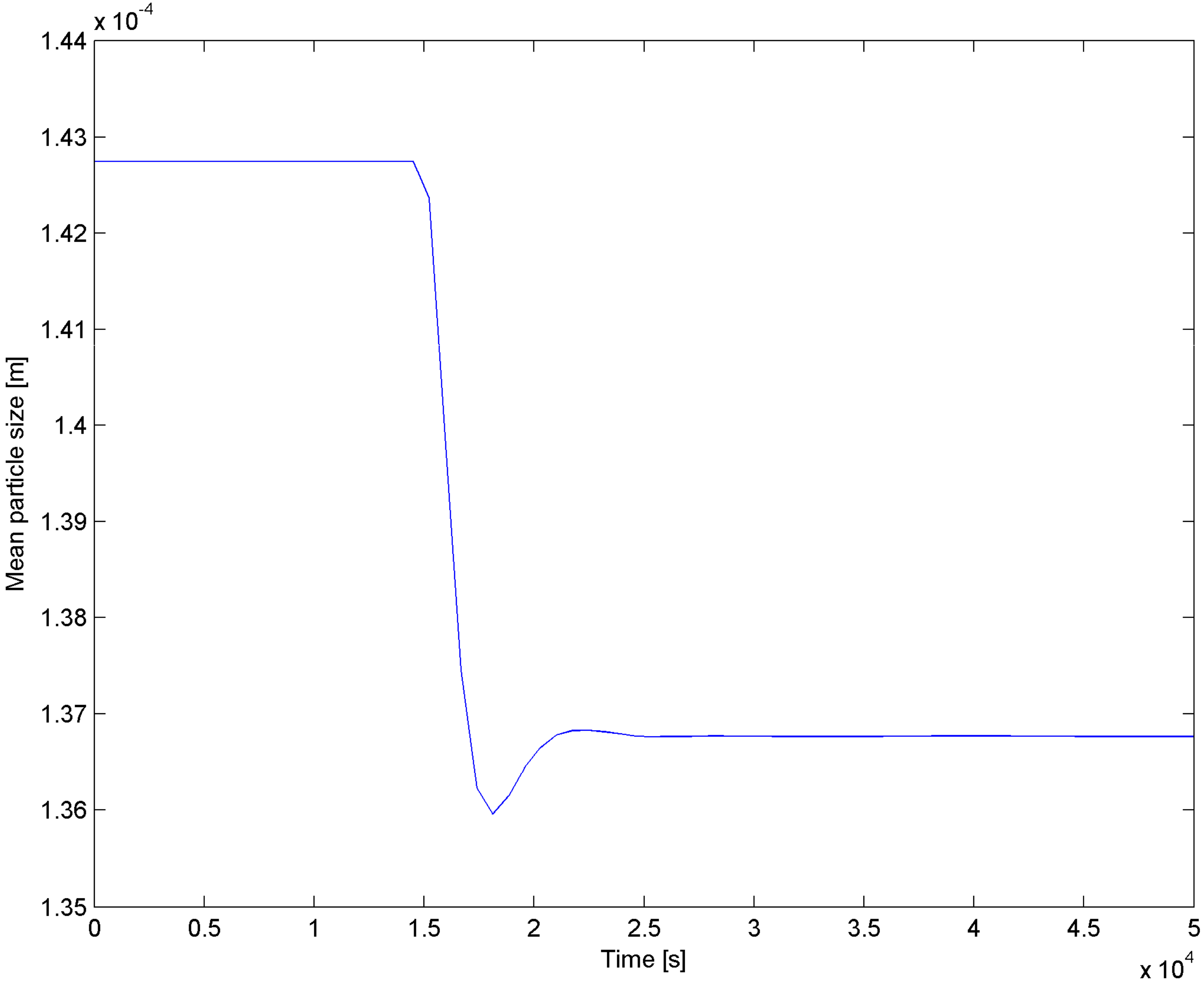
Unsteady state simulation



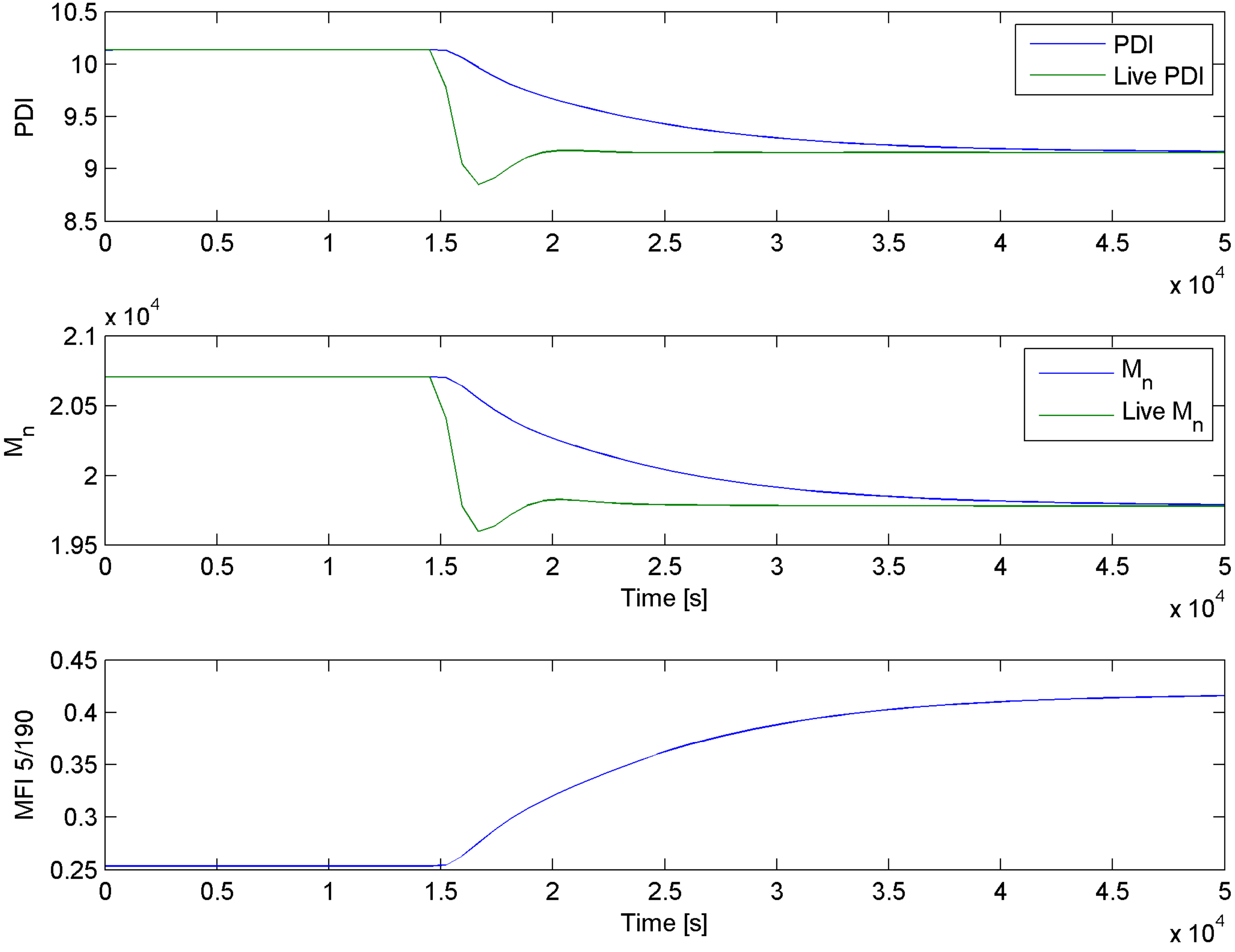
Unsteady state simulation



Unsteady state simulation



Unsteady state simulation



Unsteady state simulation

- Solution time
  - 23 s on PC running Matlab
  - 5e4 s of simulated time
  - 250 – 25 000 s for PBM models

Conclusions

- Unsteady-state reactor model
  - Segregation approach vs PBM
  - Computational efficiency
  - Kinetic scheme based on experimental data

- Comparison of industrial data and model predictions

Conclusions

- Discrepancies in polymer properties
  - Unrealistic monomer conversion

- Non-ideal mixing
  - Tanks-in-series
  - Significant effect
  - Further study required

Conclusions

- Unsteady-state operation
  - Response to step change
  - 23 s of computation time
  - Potential for application to control

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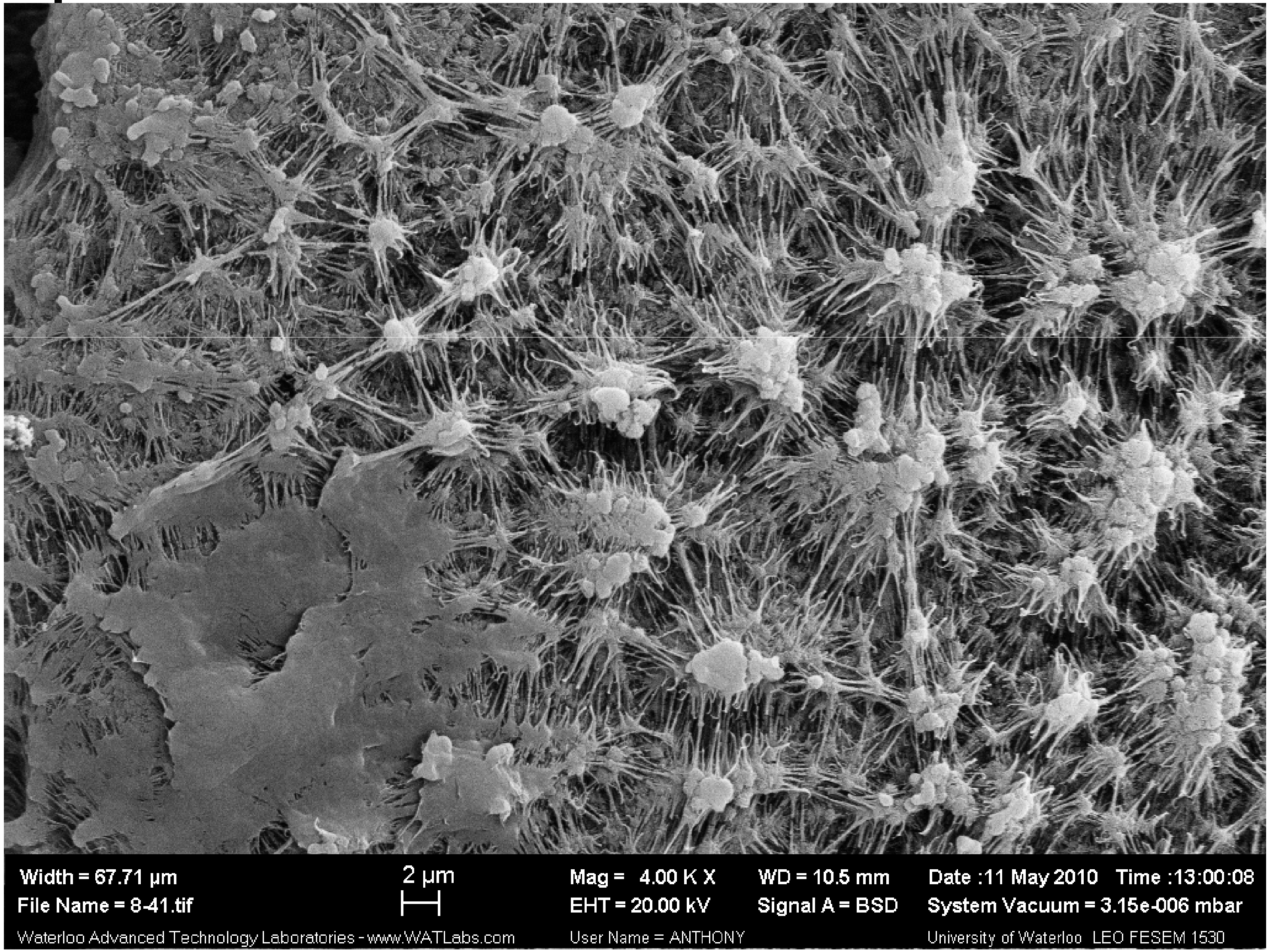
Questions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University of Waterloo LEO FESEM 1530

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