Optimization For Grade Transitions In Polyethylene Solution Polymerization

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Background
LLDPE






- **Linear low-density polyethylene (LLDPE)**
- **Made by copolymerization of ethylene with longer-chain olefins (octene, butene, hexene, propylene)**
  - Long linear molecules
  - Short chain branches

- **Has a narrower main chain molecular length compared to LDPE**
- **Has penetrated almost all traditional markets of polyethylene**

Background
LLDPE Solution Polymerization

- **Long loop with heat exchangers**
- **Continuous operation**
- **Multiple feed positions**
- **Feed includes:**
  - Ethylene
  - Comonomer
  - Catalyst (typically metallocene) with solvent
  - Hydrogen
- **Temperature and pressure are controlled to keep all components in liquid phase.**
- **Recycle ratio influences the reactor performance.**
  - Behaves like a continuous stirred-tank reactor (CSTR) when recycle ratio is high.

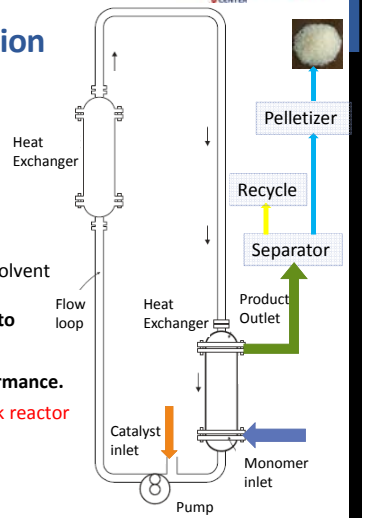


Figure source: Kao, C.I. *et al.*, EP 0891381, 2006.

Project Overview
Motivation and Objectives

Current Practice

- Different grades produced in **a single production line**
- Grade transition takes **a long time** (typically more than 3 hours)
- **Frequent grade transitions** due to high inventory cost
- **Model-based control** applied to calculate setpoint
- **PID** controller for flowrate and temperature control
- Hard to implement complex transitions; Room for improvement

Objectives

- Develop a model based control and optimization framework to
  - Minimize **transition time**
  - Minimize **offgrade products**
  - Minimize **raw material usage**

Potential Value

- **Reduction** in transition time
- **Complex** transitions are guided
- Increased **flexibility** in production wheel

Project Overview
Project Timeline and Progress

Model development
- Mass and heat balance equations
- Moment model and property correlations to predict density and MI
- Surrogate model development to predict bubble pressure
- Recycle streams introduced as a time delay model

Offline Dynamic Optimization
- Define objective function
- Case studies on hypothetical problem
- Identify process constraints

Model-Based Control

Model Development
Reactions

Chain initiation	$P_0 + M_i \Rightarrow P_{1,i}$	rate constant K_p
Chain propagation	$P_{n,i} + M_j \Rightarrow P_{n+1,j}$	rate constant K_p
Chain transfer		
• **to hydrogen**	$P_{n,i} + H_2 \Rightarrow P_0 + D_{n,i}$	rate constant K_{CH}
• **to cocatalyst**	$P_{n,i} + \mathrm{A} \Rightarrow P_0 + D_{n,i}$	rate constant K_{CA}
• **to solvent**	$P_{n,i} + \mathrm{S} \Rightarrow P_0 + D_{n,i}$	rate constant K_{CS}
• **to transfer agent**	$P_{n,i} + \mathrm{T} \Rightarrow P_0 + D_{n,i}$	rate constant K_{CT}
• **to monomer**	$P_{n,i} + M_j \Rightarrow P_{1,j} + D_{n,i}$	rate constant K_{cm}
• **spontaneous**	$P_{n,i} \Rightarrow P_0 + D_{n,i}$	rate constant K_{csp}
Site deactivation		
• **by poison**	$P_{n,i} + \mathrm{X} \Rightarrow C_d + D_{n,i}$	rate constant K_{dx}
	$P_0 + \mathrm{X} \Rightarrow C_d$	rate constant K_{dx0}
• **spontaneous**	$P_{n,i} \Rightarrow C_d + D_{n,i}$	rate constant $\mathrm{K_{dsp}}$
	$P_0 \Rightarrow C_d$	rate constant $\mathrm{K_{dsp0}}$

Model Development
Assumptions and Variables

- **Continuous Stirred-Tank Reactor (CSTR)**
- **Assume perfect mixing**

- **Three types of variables**
  - Manipulated variables
    - ***Ethylene, comonomer, hydrogen and catalyst feed flowrates***
    - ***Inlet temperature of cooling media***
  - Output variables
    - ***Product properties: MI and density***
    - ***Process requirement: ethylene conversion and reactor temperature***
  - State variables
    - ***Concentrations and moments***

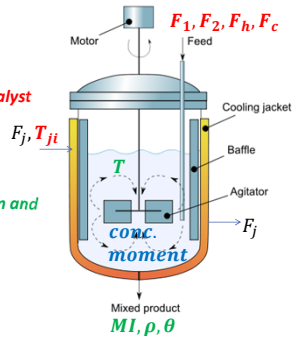


Figure source: http://en.wikipedia.org/wiki/Continuous_stirred-tank_reactor

Model Development
Method of Moments

Growing polymer chain $P_{n,i}$

Dead polymer chain $D_{n,i}$

n is the length (number of repeating units in the backbone of the polymer molecule) of the chain

i is the end group (the latest monomer adding to the chain) type

- **Live polymer moment**

$$\mu_{m,i} = \sum_n n^m P_{n,i}$$

- **Bulk polymer moment**

$$\lambda_{m,i} = \sum_n n^m (P_{n,i} + D_{n,i})$$

- **0th moment: concentrations of chains**
- **1st moment: number of repeating units**
- **2nd moment: capture distributions**

Model Development

From PC-SAFT to Kriging Model

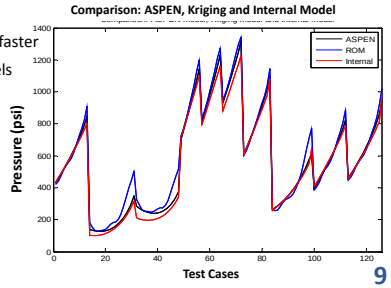
Motivation

- PC-SAFT is the most widely accepted EOS for polyethylene systems.
- But, developing and solving PC-SAFT in optimization code is hard due to its complexity.

Developed a surrogate model

- ✓ **Simple.** Monitor bubble point pressure faster
- ✓ **Easy.** Can be integrated into other models
- ✓ **Accurate.** In the region of interest

Integrated in optimization model



Baseline

Step Change Simulation

Operation conditions for two different grades

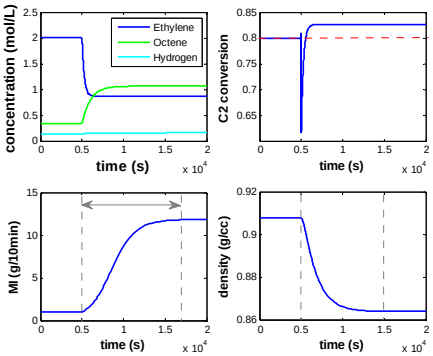
		Meaning	Units	Grade A	Grade B
Properties	MI	*Melt index*	*g/10min*	1	11.83
	Conversion	*Ethylene conversion rate*		0.8	0.826
	Density	*Density*	g/cm^3	0.908	0.864
Manipulated vars	T	*Reactor temperature*	*°C*	148.983	150
	F1	*Ethylene inlet flow*	*L/s*	0.128	0.055
	F2	*Comonomer inlet flow*	*L/s*	0.019	0.056
	Fh	*Hydrogen inlet flow*	*L/s*	0.001	0.001
	Fc	*Feed catalyst*	*mol/s*	0.00002	0.00002
Algebraic vars	Fin	*Total feed flow*	*L/s*	0.263	0.227
	Fs	*Solvent inlet flow*	*L/s*	0.115	0.115
	V	*Reactor Volume*	*L*	340	340

Step Change:

The manipulated variables are shifted from Grade A to Grade B at 5000s.

Baseline

Step Response



- Concentration of ethylene changes much faster than that of comonomer due to the difference of propagation rates.
- The ethylene conversion is required to be greater than 80%. However step response violates this bounds.
- Transition time: 3.4 hours

In the next section, we will try to reduce the transition time using the simultaneous dynamic optimization strategy.

Dynamic Optimization

Formulation and Solving Techniques

Optimization problem formulation

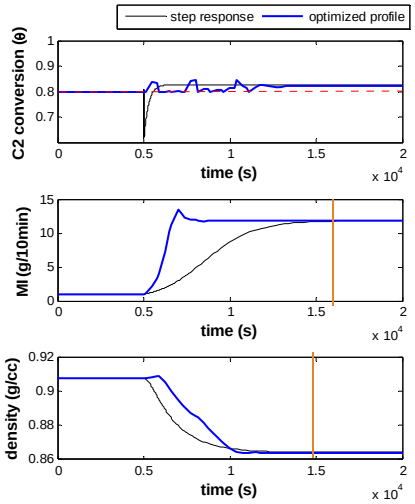
- **Objective function for obtaining optimal transition profile**

$$\min \int_0^{tf} \alpha_1 \|MI(t) - MI^*\|^2 + \alpha_2 \|\rho(t) - \rho^*\|^2 + \beta \|u(t) - u^*\|^2 \, dt$$

with constraint on ethylene conversion $\theta(t) \geq \theta^*$, u is the manipulated variable.

- This study focused on mass balance and heat balance alone, leaving VLE for future work.
- Application of 3-point collocation on 20 finite elements over 15000 seconds results in a nonlinear programming problem with 3420 variables and 3180 equality constraints.
- Using the IPOPT solver provided by GAMS, the problem was solved and the result is shown in the following slides.
- (50 finite elements were also tested, with the same accuracy.)

Optimization Result

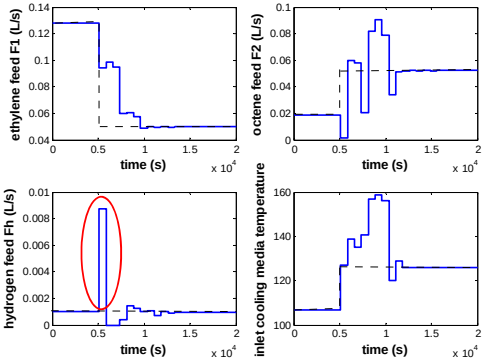


Profiles of output variables

Compared to step response

- **Ensure ethylene conversion greater than 80%**
- **Transition time is reduced from 3.4 hours to 2.2 hours.**

Optimization Result



Pros:

Better system performance

(shown in previous page)

Cons:

More complex control scheme

A spike in hydrogen feed flow rate

Chain transfer to hydrogen $P_{n,i} + H_2 \Rightarrow P_0 + D_{n,i}$

$H_2 \uparrow \rightarrow D_{n,i} \uparrow \rightarrow M_w \downarrow \rightarrow MI \uparrow$ (MI of Grade B = 11.83, MI of Grade A = 1.0)

Why complex profiles?
Characteristics of the Model

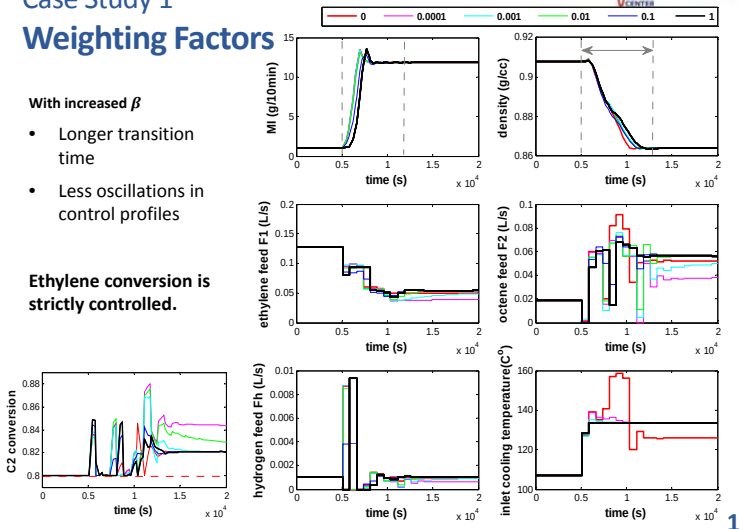
1. **High nonlinearity**
   - Rank deficiency
   - Slower convergence of the algorithm
2. **Singular control problem when $\beta = 0$ in the objective function**
   - $\min \int_0^{tf} \alpha_1 \|\mathrm{MI(t)} - \mathrm{MI}^*\|^2 + \alpha_2 \|\rho(t) - \rho^*\|^2 + \beta \|\mathrm{u(t)} - \mathrm{u}^*\|^2 \, dt$
   - Oscillatory control profiles
   - Increase β to ensure smoother profiles
3. **Path constraint**
   - The lower bound of ethylene conversion rate $\theta(t) \geq \theta^*$
   - Non-invertible high-index model when $\theta(t) = \theta^*$
   - Control profile is not smooth.

Case Study 1
Weighting Factors

With increased β

- Longer transition time
- Less oscillations in control profiles

Ethylene conversion is strictly controlled.



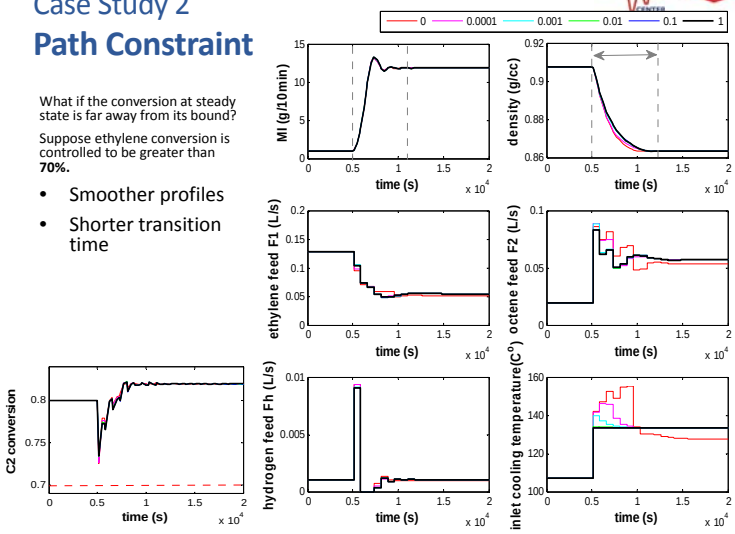
Case Study 2

Path Constraint

What if the conversion at steady state is far away from its bound?

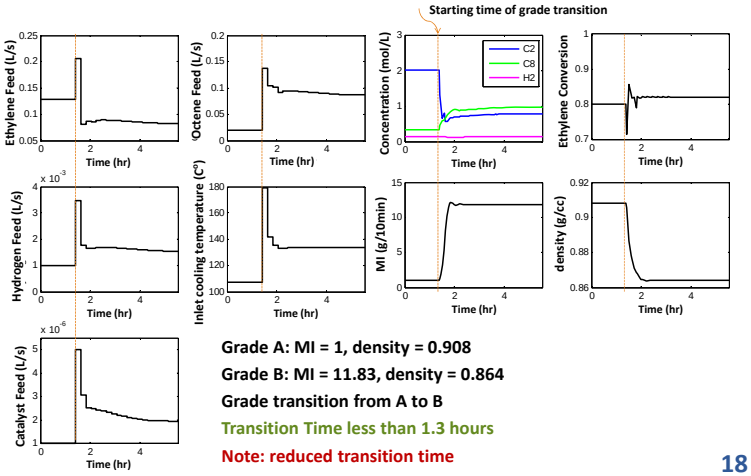
Suppose ethylene conversion is controlled to be greater than **70%.**

- Smoother profiles
- Shorter transition time



Dynamic Optimization

From high density to low density



Grade A: MI = 1, density = 0.908

Grade B: MI = 11.83, density = 0.864

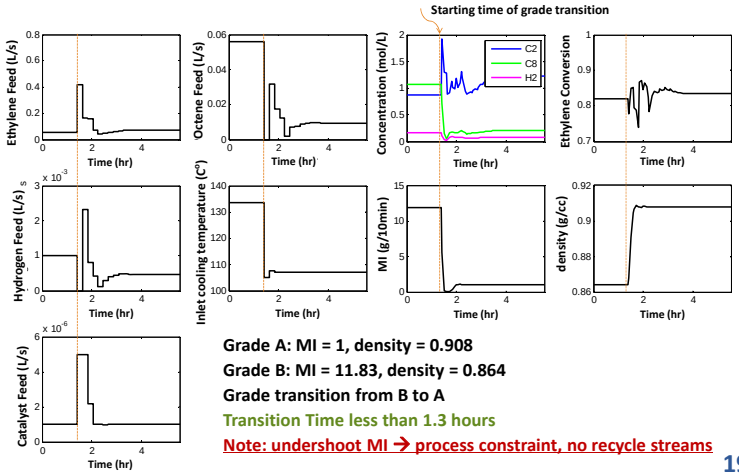
Grade transition from A to B

Transition Time less than 1.3 hours

Note: reduced transition time

Dynamic Optimization

From low density to high density



Grade A: MI = 1, density = 0.908

Grade B: MI = 11.83, density = 0.864

Grade transition from B to A

Transition Time less than 1.3 hours

Note: undershoot MI → process constraint, no recycle streams

Conclusions and Future work

- Developed a dynamic model along with moments model for property prediction and surrogate model for VLE equation
- Collocation on finite elements was applied and a better transition policy was achieved
- Incorporated recycle loop
- Identified process constraints

- Optimize the modified problem with recycle loop and process constraints taken into account
- Consider more complex kinetics with impurities and catalyst transitions
- On-line implementation issues