Model-based EVA/EVOH Continuous Process Design

Process Optimization and Development Symposium

August 20, 2013
Houston, TX
Outline

1. Problem Description
   - EVOH Process Description
   - Project Goals & Challenges

2. Problem Analysis

3. Model Description

4. Computational Methods

4. Experimental Data

5. Validation

6. Application/Case Studies
EVOH and Process Description

■ EVOH (Ethylene-vinyl alcohol copolymer) is a specialty membrane product
  □ Excellent gas and solvent barrier properties, oil and solvent resistance and transparency
  □ Applications:
    ▪ Packages and containers for foods, pharmaceuticals and cosmetics
    ▪ Plastic fuel tanks for automobiles

■ EVOH Process
  □ Step 1. EVA (Ethylene Vinyl Acetate) produced by copolymerization of ethylene and vinyl acetate

  \[
  \text{Ethylene} + \text{Vinyl acetate (VA)} \rightarrow \text{EVA}
  \]

  □ Step 2. EVOH produced by saponification of EVA

  \[
  \text{EVA} \rightarrow \text{EVOH}
  \]
**Project Goals and Challenges**

- **Project Goals:**
  1. Convert existing batch process into continuous process
     → *Lower manufacturing cost*
  2. Design continuous process recipes for grades A and B

- **Project Challenges:**
  1. No continuous process exists → *Only batch process data available*
  2. Formation of gels
     - High molecular weight off-spec products
     - Lead to costly reactor shutdown

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*Figure 1. Existing batch process for EVA*

*Figure 2. Photo of gel accumulated in the agitator*
Problem Analysis
**Gel Formation Mechanism: Hypothesis**

- Gel is a high molecular weight, cross-linked polymer formed by long-chain branching (LCB)

\[
\Delta LCB = k_{fp} [R][P] \Delta t
\]

[R], [P] are radical & polymer conc.  
\( \Delta t \) is residence time

- Effect of residence time
  - Polymer chains are formed in <1 sec
  - Some chains stay in reactor a very long time due to RTD \( \rightarrow \) more LCB

- Effect of long chains
  - Large size increases probability of attack by radical \( \rightarrow \) faster growth
  - Large size may have difficulty leaving reactor \( \rightarrow \) longer time to grow

- Gel formation is strongly dependent upon residence time distribution (RTD)
Gel Formation Control: Strategy

- **Confirm** the gel formation hypothesis by model-based experimental design
- **Reduce** the source of gel by controlling RTD through optimal process configuration
  - With increased number of CSTRs, the tail with longer residence time would be reduced
  - Cost of the reactors is also a consideration in the process design
Model Description
EVA Copolymerization Reaction Mechanism

**Initiation**

\[ I \xrightarrow{k_i} 2R \]

**Propagation**

\[
\begin{align*}
R + M_1 & \xrightarrow{k_{p11}} R_{1,0,1} \\
R + M_2 & \xrightarrow{k_{p02}} R_{0,1,2} \\
R_{m,n,1} + M_1 & \xrightarrow{k_{p11}} R_{m+1,n,1} \\
R_{m,n,1} + M_2 & \xrightarrow{k_{p12}} R_{m,n+1,2} \\
R_{m,n,2} + M_1 & \xrightarrow{k_{p21}} R_{m+1,n,1} \\
R_{m,n,2} + M_2 & \xrightarrow{k_{p22}} R_{m,n+1,2}
\end{align*}
\]

**Termination by disproportionation**

\[
\begin{align*}
R_{m,n,1} + R_{r,s,1} & \xrightarrow{k_{d11}} P_{m,n} + P_{r,s} \\
R_{m,n,1} & \xrightarrow{k_{d12}} P_{m,n} + P_{r,s} \\
R_{m,n,2} + R_{r,s,2} & \xrightarrow{k_{d22}} P_{m,n} + P_{r,s}
\end{align*}
\]

**Termination by combination**

\[
\begin{align*}
R_{m,n,1} + R_{r,s,1} & \xrightarrow{k_{c11}} P_{m+r,n+s} \\
R_{m,n,1} + R_{r,s,2} & \xrightarrow{k_{c12}} P_{m+r,n+s} \\
R_{m,n,2} + R_{r,s,2} & \xrightarrow{k_{c22}} P_{m+r,n+s}
\end{align*}
\]

**Chain transfer to polymer (LCB)**

\[
\begin{align*}
R_{m,n,1} + P_{m,n} & \xrightarrow{k_{f11}} P_{m,n} + R_{m,n,1} \\
R_{m,n,1} + P_{m,n} & \xrightarrow{k_{f12}} P_{m,n} + R_{m,n,2} \\
R_{m,n,2} + P_{m,n} & \xrightarrow{k_{f21}} P_{m,n} + R_{m,n,1} \\
R_{m,n,2} + P_{m,n} & \xrightarrow{k_{f22}} P_{m,n} + R_{m,n,2}
\end{align*}
\]

**Chain transfer to solvent**

\[
\begin{align*}
R_{m,n,1} + T & \xrightarrow{k_{f1}} P_{m,n} + T^* \\
R_{m,n,2} + T & \xrightarrow{k_{f2}} P_{m,n} + T^*
\end{align*}
\]

**Subscripts:**

- m: no of \( \text{C}_2\text{H}_4 \) units
- n: no of VAc units
- 1: \( \text{C}_2\text{H}_4 \)
- 2: VAc

**Chain transfer to monomer**

\[
\begin{align*}
R_{m,n,1} + M_1 & \xrightarrow{k_{f11}} P_{m,n} + R_{1,0,1} \\
R_{m,n,1} + M_2 & \xrightarrow{k_{f12}} P_{m,n} + R_{0,1,2} \\
R_{m,n,1} + M_2 & \xrightarrow{k_{f21}} P_{m,n} + R_{1,0,1} \\
R_{m,n,2} + M_1 & \xrightarrow{k_{f22}} P_{m,n} + R_{0,1,2}
\end{align*}
\]

**Short chain branching (SCB)**

\[
\begin{align*}
R_{m,n,1} & \xrightarrow{k_{s1}} R_{m,n,2} \\
R_{m,n,2} & \xrightarrow{k_{s2}} R_{m,n,1}
\end{align*}
\]

**Chain transfer to solvent**

\[
\begin{align*}
R_{m,n,1} + T & \xrightarrow{k_{f1}} P_{m,n} + T^* \\
R_{m,n,2} + T & \xrightarrow{k_{f2}} P_{m,n} + T^*
\end{align*}
\]

**Chain transfer to monomer**

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R_{m,n,1} + M_1 & \xrightarrow{k_{f11}} P_{m,n} + R_{1,0,1} \\
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Hierarchical EVA/EVOH Reactor Model Overview

- EVA Process Model
  - Process Outputs
    - Conversion, etc
  - Average Properties for EVA
    - Molecular Weight
    - Copolymer Composition
    - Branching Density
    - Sequence Length
  - Process Design
    - Recipe Design
    - Operational Support

- EVA/EVOH Molecular Structure Model
  - Molecular Properties for EVA/EVOH*
    - Explicit Molecular Structure
    - Molecular Weight
    - Copolymer Composition
    - Branching Density
    - Sequence Length
  - Grade Design
  - Operational Support

- EVOH Properties Model
  - Performance Properties
    - Melt Index
    - Permeability
  - Improve Properties

*EVOH properties are calculated assuming 100% scission in Saponification Step
EVA/EVOH Molecular Structure Model

- **Hybrid Stochastic Deterministic Method (HSDM)**
  - Incorporate hybrid nature of the stochastic and deterministic events exactly into the model (Figure 1)
  - Describe explicit details of molecular and morphological structure (Figure 2&3)

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**Figure 1:** Evolution of molecular and morphological properties

**Figure 2:** Explicit structure of a EVOH copolymer chain generated from the HSDM model

**Figure 3:** Example Mn and Mw distribution predicted from the HSDM model
### Process Design Procedure

<table>
<thead>
<tr>
<th>Tasks</th>
<th>Sub-tasks</th>
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<tbody>
<tr>
<td>1. Model Calibration &amp; Validation</td>
<td>a) Validate model assumptions</td>
</tr>
<tr>
<td></td>
<td>b) Calibrate model parameters*</td>
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<td></td>
<td>c) Validate calibrated model against batch process data</td>
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<td>2. Optimal Operating Policy Design</td>
<td>a) Establish qualitative &amp; conceptual operating policy design that meets process &amp; product specifications</td>
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<td>b) Model-based design of optimal operating policy for grades A and B</td>
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<td>c) Validate proposed policy with semi-batch experiments</td>
</tr>
<tr>
<td>3. Continuous Process Design</td>
<td>a) Build cost models</td>
</tr>
<tr>
<td></td>
<td>b) Reproduce optimal semi-batch operating policy with continuous process</td>
</tr>
<tr>
<td></td>
<td>c) Economic optimization with cost model</td>
</tr>
</tbody>
</table>

* RES computational methods employed for model calibration described in following slides
Computational Methods
Model Calibration & DoE Workflow

Main Features

- **Parameter Selection (Sensitivity Analysis)**
  - Identify which parameters can be estimated
  - Identify what data must be collected

- **Estimation of Best Fit (Global Estimation)**
  - Address limitations of locally optimal fit

- **Model Revision**
  - Integral to calibration; driven by data

- **Design of Experiments (DoE)**

Flowchart:

1. Model
2. Experimental data
3. Initial Comparison
4. Dominant Parameter Selection (Sensitivity Analysis)
5. Model – Data Calibration (Parameter Estimation)
6. Accept?
   - Yes: Calibrated Model
   - No: Model Revision
7. Model-based Design of Experiments (DoE)

Graph:

- Space Velocity (1/hr)
- Temperature (°C)
- Conv. 80%, Conv. 90%, Conv. 100%
- Other Conditions: Pressure, Feed Composition, Recycle Ratio, etc.

Legend:

- Model
- Existing Data
- Requested Data
**Parameter Selection: Local Sensitivity Analysis**

- **Parametric sensitivities**
  
  Differential sensitivity:
  \[
  \frac{\partial y_i}{\partial p_j}
  \]
  
  \(y_i\): variable (e.g., concentration)
  \(p_j\): parameter (e.g., rate constant)

- **Example: Output exhibits different sensitivity to the rate constants of various reactions**
  
  - (blue) Bid + C8 \(\rightarrow\) Bid:C8, \(k_f(10)=10^{-7}\)
  - (green) fret + C8 \(\rightarrow\) fret:C8, \(k_f(29)=5(10^{-8})\)
  - (red) BAR + C8 \(\rightarrow\) BAR:C8, \(k_f(4)=10^{-6}\)

- **Local sensitivities depend on the specified values of the parameters**
  
  Early in model development these values are highly uncertain \(\rightarrow\) results of local sensitivity analysis can be misleading! \(\rightarrow\) Requires **Global Sensitivity Analysis**
Global sensitivity analysis (GSA) addresses limitation of sensitivity analysis

- For each sensitivity, compute a **scalar metric**, (e.g. max, integral of trajectory, etc)

- Sample many different parameter values and average metric

Random sampling from user-defined parameter space

Perform sensitivity analysis from each sample, compute metric and statistics

Sensitivity results contain information across a wide range of parameter values
Global Parameter Estimation: Finding the Best Possible Fit

- (Local) Parameter estimation often converges to different solutions depending on the initial guess for the parameter values.

- Several strategies have been developed to ensure the best possible fit is obtained, e.g., *Multi-Start Parameter Estimation*.

Example:

Local Fit (poor) vs. Global Fit

![Local Solution vs. Global Solution](image)

6,561 estimations
~5 hr on 500-node cluster

Kim et al., BMC Bioinformatics 2010, 11:202
Experimental Data
Experimental Data: EVA Conversion and Mw

- EVA conversion data was captured to describe the progress of the polymerization
- Conversion was converted from calorimetric data

\[ x(t) = \frac{\int_0^t Q dt}{\int_0^{t_f} Q dt} \]

\( t_f \) is the final time

- Molecule weight data captured using GPC
  - Molecular weight distribution
Experimental Data: Ethylene/VA Content

- Ethylene/VA content provide key information to understand the reactivity of ethylene and VA monomers in the co-polymerization.

\[ \text{ETY}_{\text{mole}}\% = \frac{n}{m+n} \cdot 100\% \quad \text{ETY}_{\text{mass}}\% = \frac{n \cdot MW_{VA}}{m \cdot MW_{C_2H_4} + n \cdot MW_{VA}} \cdot 100\% \]

\[ \text{VA}_{\text{mole}}\% = 1 - \text{ETY}_{\text{mole}}\% \quad \text{VA}_{\text{mass}}\% = 1 - \text{ETY}_{\text{mass}}\% \]

- It is typically acquired by IR or Raman spectroscopy [Shimoyama, et al, 1997]

Validation Results
Model Validation

- Excellent agreement for conversion and ethylene content
- Good agreement for number and weight average MW (Mn & Mw)

![Graph showing data comparison](image1)

![Graph showing data comparison](image2)
Case Studies
Continuous Process Design (including start-up)
- **Batch**: initial charge of EVA and initiator to the reactor and start reaction
- **Semi-batch**: start to add additional EVA and initiator (Flow In)
- **Continuous**: start the outlet flow (Flow Out)
Yield, Mn, Mw was predicted from the kinetic model

Although it only took 10~15 hrs for yield to reach steady state, it took about 100 hrs for the Mw to reach steady state.

One of the potential future process design target would be minimizing the start-up time ➔ reduce the amount of off-spec product
EVA Ethylene Content and Monomer Sequence

- Ethylene Content and Monomer Sequence are almost constant over the whole process
- This is expected as the propagation is controlled by the monomer reactivity ratios ($r_1, r_2$)

\[ r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}} \]

\[
\begin{align*}
R_{m,n,1} + M_1 &\xrightarrow{k_{p11}} R_{m+1,n,1} \\
R_{m,n,1} + M_2 &\xrightarrow{k_{p12}} R_{m,n+1,2} \\
R_{m,n,2} + M_1 &\xrightarrow{k_{p21}} R_{m+1,n,1} \\
R_{m,n,2} + M_2 &\xrightarrow{k_{p22}} R_{m,n+1,2}
\end{align*}
\]
Simulation of Molecular Structures in Various Time Points

EVA Yield

- Batch
- Semi batch
- Continuous

5000 molecules at steady state of continuous mode

- 5000 molecules at 0.5hr of Batch mode
- 5000 molecules at 2hr of Batch mode
- 5000 molecules at 3.5hr of Batch mode

Page 27 - Confidential Information
Example of Explicit Molecular Structure in Batch (1/3)

- 50 out of 5000 simulated molecules at 0.5hr Batch

Molecule 1  Molecule 2  Molecule 3  Molecule 4  Molecule 5  Molecule 6  Molecule 7  Molecule 8  Molecule 9  Molecule 10

Molecule 11  Molecule 12  Molecule 13  Molecule 14  Molecule 15  Molecule 16  Molecule 17  Molecule 18  Molecule 19  Molecule 20

Molecule 21  Molecule 22  Molecule 23  Molecule 24  Molecule 25  Molecule 26  Molecule 27  Molecule 28  Molecule 29  Molecule 30

Molecule 31  Molecule 32  Molecule 33  Molecule 34  Molecule 35  Molecule 36  Molecule 37  Molecule 38  Molecule 39  Molecule 40

Molecule 41  Molecule 42  Molecule 43  Molecule 44  Molecule 45  Molecule 46  Molecule 47  Molecule 48  Molecule 49  Molecule 50
50 out of 5000 simulated molecules at 2hr Batch

Example of Explicit Molecular Structure in Batch (2/3)
Example of Explicit Molecular Structure in Batch (3/3)

- 50 out of 5000 simulated molecules at 3.5hr Batch
Example of Explicit Molecular Structure in CSTR

- 50 out of 5000 simulated molecules at steady state of CSTR

Detailed structure is shown in next slides
**Molecule 2**
Recipe: CSTR
No. of branches = 4
Degree of polymerization = 5750
Averaged C2H4 content = 0.469
Averaged C2H4 sequence length = 1.3
Averaged VAc sequence length = 1.6
Detailed Structure: Branch Points

Molecule 4
Recipe: CSTR
No. of branches = 26
Degree of polymerization = 15660
Averaged C2H4 content = 0.457
Averaged C2H4 sequence length = 1.3
Averaged VAc sequence length = 1.6

Black circle: branch point
EVA: Evolution of MW and Ethylene Content Distribution

- Animation* showing evolution from 0.1 – 3.5 hour during batch operation

* Select “Slide Show” mode to view the animation
Molecular weight distribution (MWD) widens over time from batch mode to CSTR mode
- At CSTR steady state, MWD is widest
- Ethylene content distribution has no significant trend
The distribution is shifting to high molecular weight as the reaction time evolves.
Comments on EVA Gel Amount Estimation

- **Gel amount estimation**
  - Gel can be defined as high molecular weight branched polymer molecules formed by long-chain branching (see below for an example).
  - Gel amount may depend on process operating conditions, such as temperature and solvent, therefore calibration with experimental data is needed.

![Molecular Weight Distribution](image1)

- Degree of Polymerization = 86,288
- No. of Branches = 112
Process Design: **Effect of Residence Time Distribution**

- With increased number of CSTR, gel amount is greatly reduced due to improved residence time distribution (the tail with long residence time is eliminated/reduced)

* Both cases (1-CSTR and 8-CSTRs) use the same condition and total residence time
Reactor configuration with 2-CSTRs series were recommended

- CSTR series with 1 to 8 reactor were evaluated based on gel amount, conversion and construction and operation cost.
Summary

- A continuous reactor with 2-CSTR in series was designed for the EVA process from existing batch process data
  - The process model including EVA kinetics and molecular structural model was developed and calibrated against existing data from batch reactor
  - The model was applied to design a first-of-the-kind continuous reactors, in addition to addressing the gel problem found in the process

- Additional applications utilizing the models are in progress, including:
  - 1. Optimize start-up procedure and grade transition design to minimize the off-spec product
  - 2. Safety study to identify key process disturbances that may cause safety and operational concerns and recommend counter-measures
  - 3. Generate a platform for plant operator training and simulate different scenarios with abnormal conditions