Implementation of Complex Low-Density Polyethylene Chemistry into Rigorous Computational Fluid Dynamics Model

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Outline

- Introduction
- Objective
- Verification plan
- Methods
- Results
- Conclusions

Low-Density Polyethylene (LDPE)

- Soft, flexible, and lightweight plastic material
  - Commonly used for orthotics, prosthetics, bottles, plastic bags, and food packaging
- The U.S. produces over 3,00 metric tons a year [1]
  - Global market size over US$ 40 billion [2-6].
- Highly competitive market
  - Manufacturers want to reduce cost, reduce waste, and increase production efficiency

LDPE Simulation

- Simulating LDPE reactors reduces cost, reduces waste, and increases production efficiency
  - Reduces time and cost for Research and Development
    - Determines properties of polymer
  - Diagnose and prevent problems
  - Shows conditions within the reactor

Simulation Methods

- There are many polymer simulation software
  - Aspen's Polymer Plus, gPROMS, POLYRED, and Predici [7-10]
  - Proven to match plant reactors [7-10]
- Can only produce polymer properties
  - Assume Continuous Stirred Tank Reactor (CSTR)
  - Perfect mixing

Computational Fluid Dynamics (CFD)

- CFD can improve LDPE simulations
  - Can simulate chemistry similar to other software
  - Can also approximate non-ideal mixing in the reactor
  - Can create reactor geometries closer to reality
  - Can see behavior in the reactor and perform Research and Development

Objective

- To incorporate complex LDPE chemistry into a rigorous CFD model
  - To investigate micromixing effects on Molecular Weight Distribution (MWD)
- Others have used simple chemistry or simple CFD models [11-13]

Why MWD is Important

- MWD often determines category of polyethylene
- Determines most mechanical properties
  - Tensile strength
  - Density
  - Melting temperature
  - Toughness

Verification Plan

Step	CFD	Chemistry	Temperature	Baseline
1	CSTR	Simple	1	Aspen
2	CSTR	Complex	1	Aspen
3	CSTR	Complex	2	Aspen
4	Full Reactor	Complex	1	Plant Reactor

Chemistry Schemes

- Simple Chemistry:
  - Initiation, propagation, and termination
- Complex Chemistry:
  - Adds polymer branching, chain transfer, and scission reactions
  - Reaction equations are omitted at the request of the sponsor
- Reaction rates take on general Arrhenius expressions
  - $k = Ae\text{^}(E_a/RT)$

Chemical Source Terms

- Rate of production/consumption
  - Sum of production/consumption rate for all reactions
  - Example:

1. $P_3 + M \xrightarrow{k_P} P_4$
2. $P_4 + M \xrightarrow{k_P} P_5$

$$- S_{P_4} = \frac{dP_4}{dt} = k_P[P_3][M] - k_P[P_4][M]$$

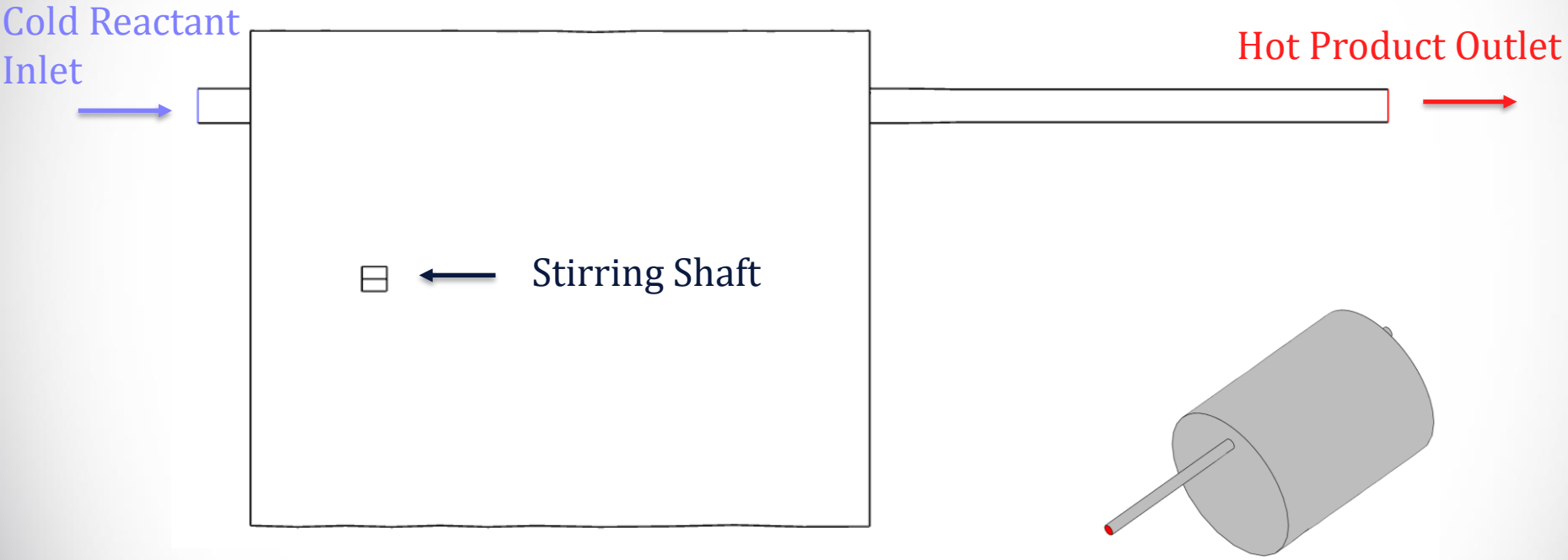
Polymerization Problems

- Need chemical source terms for every species
  - Also for each chain length of polymer
  - Theoretically infinite
- Can use statistical quantities called moments
  - $\mu_i = \sum_{n=1}^{\infty} n^i [P_n]$
  - Reduces the computational rigor

MWD Calculations

- Indicators of the Molecular Weight Distribution (MWD):
  - Number average molecular weight
  - Weight average molecular weight
  - Polydispersity Index
  - Frequency of Long Chain Branches (LCB)
  - Frequency of Short Chain Branches (SCB)

CSTR Model



Full Reactor Model

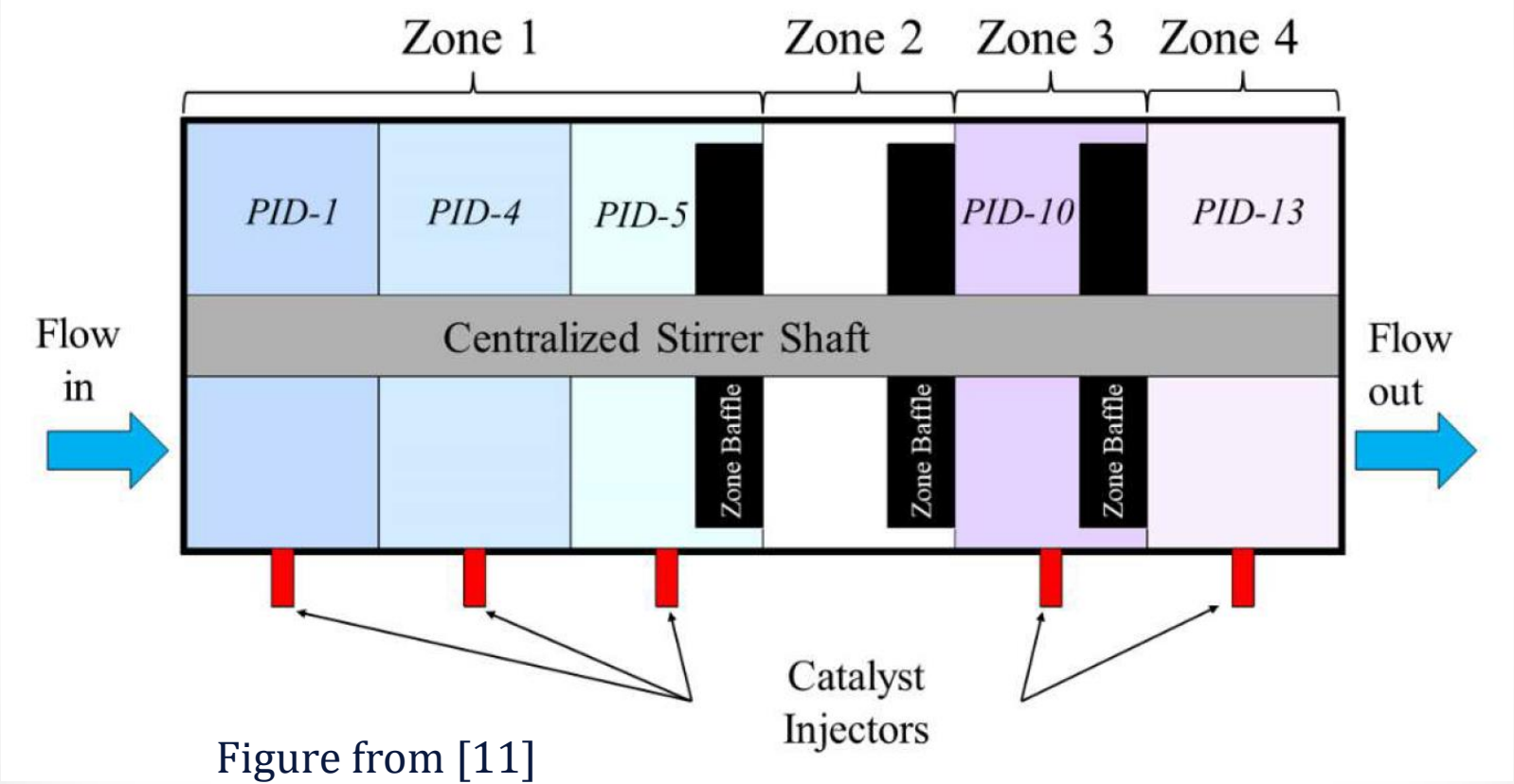
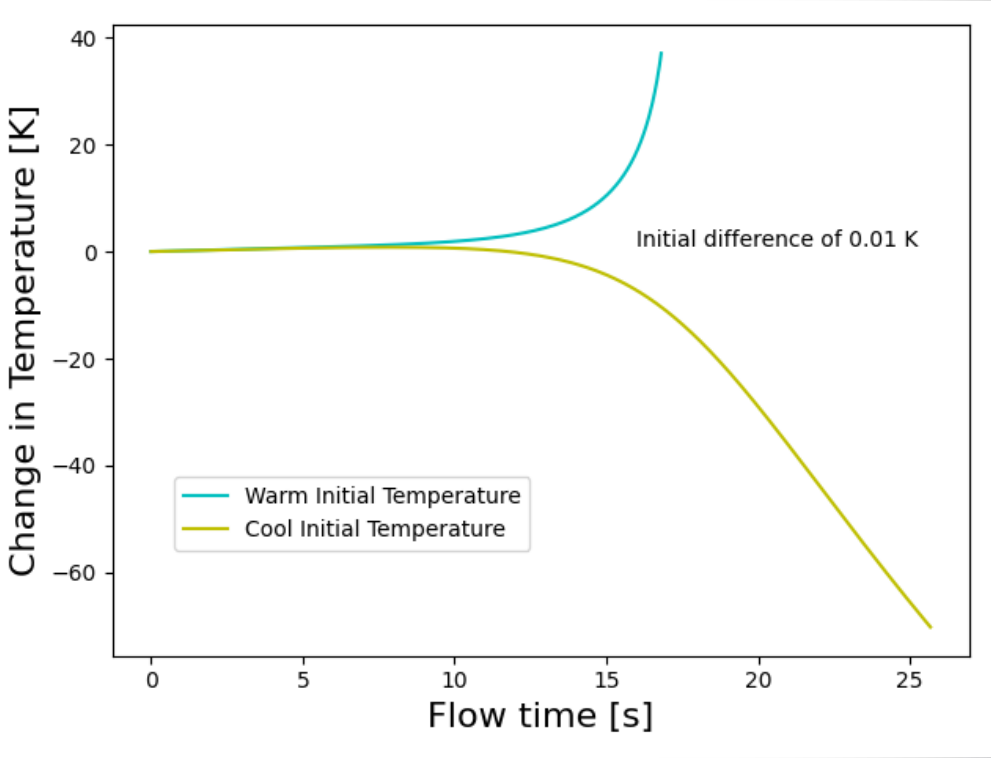


Figure from [11]

Step 1 Results

- Initially had trouble:
  - Temperature dependent and autoaccelerating chemistry
  - Numerical instability from stiff chemistry and simple model
  - Short residence times
- A PID controller was necessary to obtain a steady solution



Step 1 Results

- Simple model, simple chemistry, and initial temperature 1 compared to polymer software

Quantity	Temperature	Initiator	Monomer	Polymer
% Difference	0.01%	0.43%	0.01%	0.02%
Quantity	Termination Reaction Rate	Number average MW	Weight Average MW	Polydispersity Index
% Difference	0.00%	0.02%	0.03%	0.02%

Step 2 Results

- Simple model, complex chemistry, and initial temperature 1 compared to polymer software

Temperature	Initiator 1	Initiator 2	Monomer	Polymer	Agent
0.00%	0.47%	0.36%	0.03%	0.15%	0.00%
Termination Reaction Rate	Number Average MW	Weight Average MW	Polydispersity Index	Short Chain Branching	Long Chain Branching
0.23%	0.00%	2.15%	2.15%	0.07%	0.40%

Step 3 Results

- Simple model, complex chemistry, initial temperature 2 compared to polymer software

Temperature	Initiator 1	Initiator 2	Monomer	Polymer	Agent
0.00%	0.44%	0.31%	0.01%	0.05%	0.00%
Termination Reaction Rate	Number Average MW	Weight Average MW	Polydispersity Index	Short Chain Branching	Long Chain Branching
0.47%	0.01%	1.74%	1.73%	0.21%	0.53%

Step 4 Results

- Not finished yet
  - Chemistry is being implemented one zone at a time
    - Only zone 1 has been implemented
  - Can only compare results to outlet values of the plant reactor
    - Values are similar to the CSTR

Conclusions

- Step 1: correct CSTR model with PID control
- Step 2: complex chemistry has been implemented correctly
- Step 3: complex chemistry works for multiple conditions
- Step 4: indicates complex chemistry has been implemented correctly

Future Work

- Implement complex chemistry into the entire reactor
- Add complexities:
  - Variable material properties
  - MWD calculation
- Study non-ideal micromixing
- Optimize reactor
- Perform R&D
- Include more chemical complexities:
  - Gel effect
  - Multiradical sites
  - Topological scission

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Questions

CSTR CFD Settings

- Mesh Size: 6.5e4 cells
- Timestep: 0.1 sec.
- Turbulence Model: Standard k $-$ ϵ
- Species Model: Species Transport
- Pressure-Velocity Coupling: Simple
- Spatial Gradient: Least Squares Cell Based
- Discretization:
  - Pressure: Simple
  - Agent and Monomer: Second Order Upwind
  - Momentum, Turbulent Kinetic Energy, Turbulent Dissipation Rate, and all other species: First Order Upwind
- Underrelaxation factors:
  - Pressure: 0.3
  - Turbulent Kinetic Energy and Turbulent Dissipation Rate: 0.8
  - Momentum: 0.1
  - Density, Body Forces, and all species: 1

Full Reactor CFD Settings

- Mesh Size: 5.7e6 cells
- Timestep: 1.32e-3 sec.
- Turbulence Model: $k-\omega$ SST
- Species Model: Species Transport
- Pressure-Velocity Coupling: Simple
- Spatial Gradient: Least Squares Cell Based

- Discretization:
  - Pressure: PRESTO!
  - Momentum, Species, and Energy: QUICK
  - Polymer Moments: Second Order Upwind
  - Turbulent Kinetic Energy and Turbulent Dissipation Rate: First Order Upwind
- Underrelaxation factors:
  - Pressure: 0.5
  - Turbulent Kinetic Energy and Turbulent Viscosity: 0.75
  - Turbulent Dissipation Rate: 0.8
  - Momentum: 0.5
  - Species and Energy: 0.95
  - Density, Body Forces, and Polymer Moments: 1