April 25, 2018

Dr. John Hedengren
Brigham Young University
350 Clyde Building
Provo, UT 84602

Dear Dr. Hedengren,

Our team has had the opportunity to research polymer reactions in fluidized bed reactors for the past weeks. We are, therefore, pleased to submit our final report, which includes our findings and the simulation and control of a simplified reactor model.

Fluidized bed reactors are widely used in industry for polymer production. The demand for polymers have increased drastically in the past years and there are no signs of slowing down. Innovative applications and cheaper production methods are contributors to this increasing demand. Therefore, the development of optimal controllers is desirable to optimize polymer production while minimizing costs, off spec products, risks, energy usage, and environmental impact.

The main contributions of the attached report are:

- A model based on reaction kinetics and mass balances.

- The simplification of the method of moments by the use of melt index correlations.

- Polypropylene melt index sensitivity to hydrogen, propylene, and butene mass flow rate changes.

- Strategies of control of a simplified reactor model.

Finally, we would like to thank you for the opportunity of researching such an interesting application of dynamic optimization and for all the help extended throughout the semester.

Best Regards,

Clifton Anderson, Guilherme de Oliveira, and Ben Horne

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Clifton Anderson, Guilherme de Oliveira, Ben Horne, Reza Abbasi, Miriam Lopez

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Abstract

A dynamic model of a polypropylene reactor is developed to analyze the reaction dynamics of polymerization in a fluidized bed reactor. A brief review of polyolefin models and optimization is presented and plans are made for the dynamic model. The dynamic model's melt index is shown to respond differently to changes in hydrogen, monomer, and comonomer amounts fed. Increasing hydrogen feed changes melt index by 0.357 ($\frac{g/10min}{kg/hr}$). Monomer and comonomer changes cause opposite effects in the melt index, $-10*10^{-5} vs - 2.9*10^{-5} (\frac{g/10min}{kg/hr})$, respectively. Optimal solutions are found for the dynamic model controller and details for future work are laid out.

1 Introduction / Literature Review

Polyolefin (PO) production in fluidized bed reactors (FBR) is one of the most common reaction schemes in PO production. FBRs are complex systems, and the final PO properties depend on the reactor conditions. Fluidization occurs when a liquid or gas flows through a catalyst bed quickly enough for the solids to move and flow. There is a minimum velocity required to lift the particles and different flow regimes, such as bubbles and entrainment, appear as the vapor velocity increases. In a PO FBR, ethylene or propylene are mixed with a small amount of co-monomer (often 1-butene or 1-hexene) to adjust the polymer properties.

A robust model of an FBR should describe the process on a range of scales. There are three physicochemical aspects of an FBR system that may be modeled: chemical kinetics, heat transfer and fluid mechanics, and overall dynamic behavior. Each of these is important on a different scale. Kinetics describe the microscale molecular movement. Fluidization and characterization of the flow regimes ranges from microscale to mesoscale. Dynamic modeling of the entire reactor, including production and scheduling, is macroscale, involving bulk materials and long durations. In the early 1990's, McAuley developed hydrodynamic and kinetic schemes that have been widely used. They used their model in predictive control to optimize a transition between polymer grades. Reza Abbasi et al. created a dynamic model that predicted the reactor temperature, polymer density, and melt index (MI) for a small pilot reactor. It considered the hydrodynamics and heat transfer of an industrial FBR for PE production that accounted for both an emulsion and a bubble phase, with reaction occurring in each. The model also used rate equations for a Ziegler-Natta insertion catalyst with the method of moments, a deterministic approach to predicting polymer molecular weights, to predict the final polymer MI as a function of monomer and comonomer concentrations. This model predicted grade transitions on the order of hours.

Many FBRs are convectively cooled by the specific heat of reactant flow inside the reactor or by cooling jackets outside, but a more recent method takes advantage of latent heat by introducing a condensable gas into the feed stream. Droplets of this gas (such as pentane) vaporize in the reactor and are recondensed up to about 50% in a heat exchanger before re-entering the reactor. This inert has a benefit over more common non-condensable gases, like Nitrogen, for its cooling ability. However, modeling condensation involves discontinuous temperature responses that often prove intractable for gradient-based solvers. In the literature, there are no reports of an optimal grade transition using a condensed phase heat exchanger. In addition, many robust models are too complicated for reliable control. This report presents a first step toward a controllable model by using simplified kinetics and mass balances.

2 Theory and Methods

The model dynamically predicts polymer production rate using ab initio equations. The main state variables are the vapor mass fractions and are modeled by first-order mixing with a consumption term, as shown in Equation 1.

$$M_{vapor}\frac{dx_i}{dt} = -x_i * m_{out} + (m_{in} - r_{cons}) \tag{1}$$

M_{vapor} is the total mass flow rate of the vapor inside the reactor, x_i is the component mass fraction, m_{out} is the outlet vapor flow rate, m_{in} is the inlet component mass flow rate. $R_{prop,i}$ is the propagation rate of monomer and comonomer (It may not always be clear what is monomer and what is comonomer). All mass fractions were forced to a sum to unity. The form of the R_{cons} term varies by component, and is shown in Equations 2-5

$$r_{prop,C3} = -k_{p,C3} * y_{C3} * y_{catalyst} * e^{-E_{prop,C3}/RT} \tag{2}$$

$$r_{prop,C4} = -k_{c,C4} * y_{C4} * y_{catalyst} * e^{-E_{prop,C4}/RT} \tag{3}$$

$$r_{chain,H_2} = -k_{ct,H_2} * y_{H_2} * y_{catalyst} * e^{-E_{chain}/RT} \tag{4}$$

$$r_{deact} = -k_d * y_{catalyst} * e^{-E_{deact}/RT} \tag{5}$$

Where the reaction is first-order with respect to both component and catalyst concentration. R_{chain} is the molar consumption rate of hydrogen, where a live chain is terminated and the catalyst site can initiate another chain. R_{deact} is the catalyst deactivation rate, account in general for effects like poisoning. This reaction allows the model to account for poisons in the stream without including them in the balances. Furthermore, the rates assumed Arrhenius behavior, though temperature responses were not considered in this report. The mass production rate is the sum of the reacting component consumption term multiplied by its molecular weight, as shown in Equation 6

$$r_{poly} = \sum(r_i * MW_i) \tag{6}$$

$$i = C3, C4, H_2$$

The melt index (MI) property was modeled as a quadratic that depended on a ratio of H_2 to monomer and comonomer. This is shown in Equations 7-8:

$$MI = a * x^2 + b * x + c \tag{7}$$

$$x = \frac{y_{H_2}}{y_{C2} + y_{C4}} \tag{8}$$

Where a, b, and c were provided without an explicit domain or range. To avoid extrapolation, we chose an upper melt index of 50 g/10min and a hydrogen-to-olefin ratio of 0.0334.

A summary of variable types is shown in Table 1:

Table 1: Variables distributed in controlled variables (CVs), state variables (SVs), and manipulate variables (MVs)

CVs	MI
SVs	y_{C3}, y_{C4}, y_{H_2}, $MI_{instantaneous}$
MVs	$\dot{m_{C3}}$, $\dot{m_{C4}}$, $\dot{m_{H_2}}$

3 Simulation and Sensitivity Analysis

Doublet tests for the reagent flow rates were carried out in simulation mode to explore the production rate and melt index sensitivities. Only 1 MV was varied at a time. Below, three different simulations are presented followed by a brief discussion.

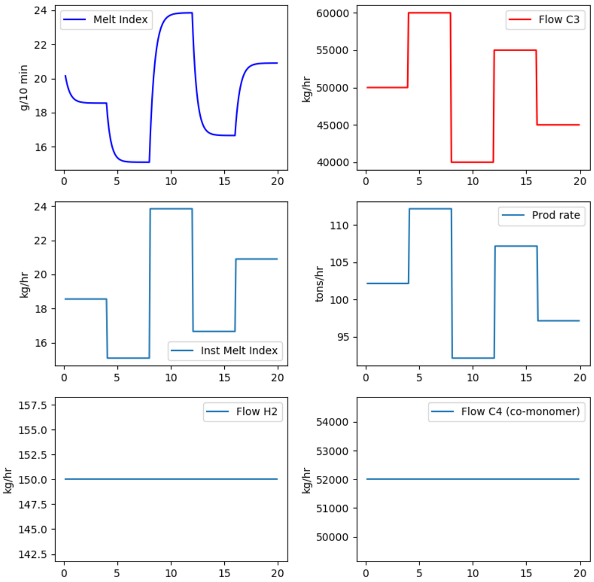

Figure 1: Propylene Doublet Test Simulation. Propylene feed (MV) is manipulated (graph in the top right) while butene and hydrogen feeds are maintained constants (graphs in the bottom). Melt Index (CV) response is seen in the top left. Production rate is portrayed in the middle to the right and instantaneous melt index in the middle to the left.

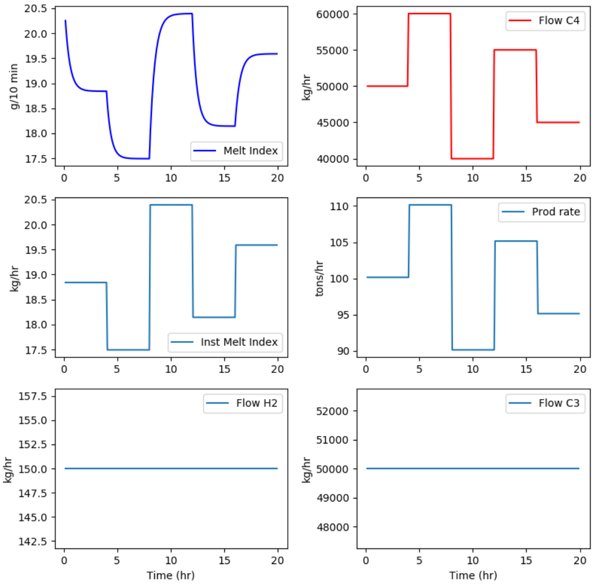

Figure 2: Butene Doublet Test Simulation. Butene feed (MV) is manipulated (graph in the top right) while propylene and hydrogen feeds are maintained constants (graphs in the bottom). Melt Index (CV) response is seen in the top left. Production rate is portrayed in the middle to the right and instantaneous melt index in the middle to the left.

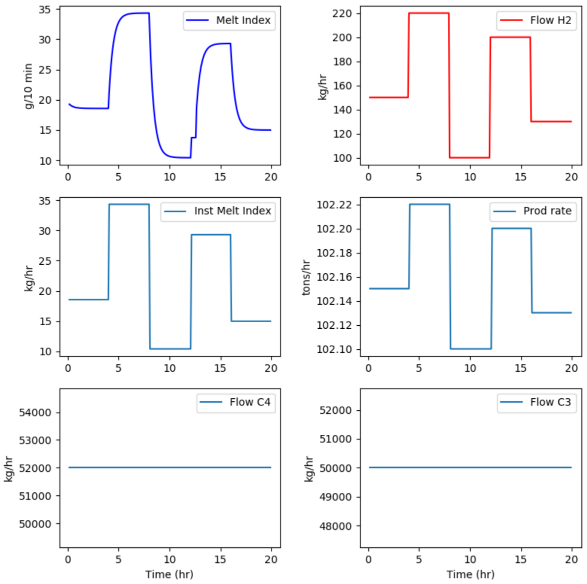

Figure 3: H_2 Doublet Test Simulation. H_2 feed (MV) is manipulated (graph in the top right) while propylene and butene feeds are maintained constants (graphs in the bottom). Melt Index (CV) response is seen in the top left. Production rate is portrayed in the middle to the right and instantaneous melt index in the middle to the left.

Figures 1 and 2 show, respectively, the doublet tests conducted for C3 and C4. There are three important things to notice from these graphs. First, the MI moves opposite to C3 and C4. Second, the MI gain for C3 is higher than for C4 ($-10 * 10^{-5}$ vs $-2.9 * 10^{-5}$ ($\frac{g/10min}{kg/hr}$)). Third, the production rate gain is equal for both monomers. This is expected, given that the production rate is linear with respect to C3 and C4 through first-order kinetics. Furthermore, the ratio used in the MI correlation depends only on the sum of C3 and C4. Thus, unconstrained by other material properties, any combination of flow rates for a given MI can be used to control the production rate.

Hydrogen responds differently because it is involved differently in the calculation of both MI and production rate. Figure 3 shows the hydrogen doublet test. There are three important things to notice and one important observation to be drawn from this graph. First, the response of the CV is directly proportional to MV movement. Second, the gain is 0.357 ($\frac{g/10min}{kg/hr}$), which is about 10,000 times greater in magnitude than either of the monomers. Third, the production rate is also directly proportional to MV movements (similar to the scenarios above).

The extreme difference in sensitivity between hydrogen and the hydrocarbons can be explained by the sensitivity of the empirical correlation. The correlation is second-order with respect to hydrogen, but inversely proportional to the square of the olefin concentrations. Because of this sensitivity, a controller with narrow dead bands is especially desirable in the H_2 feed, otherwise considerable fluctuation will be seen in the polymer's MI. Also, H_2 feed accounts for less than 0.2% of the inlet mass flow; therefore, what appears to be a small overall change to the mass flow, can signify the production of highly off spec products.

4 Control

Using our simple model, a controller was implemented using model predictive control (MPC) with varying setpoints. Maintaining a simplified model with estimated parameters is helpful for enabling the control of the system. Simulations can be done using more detailed, accurate models, but controlling detailed systems with MPC can be difficult because of their unsteady and complex nature.

Initially the controller could achieve the setpoint, but the MVs (especially C3 flow), would jump considerably to achieve the value. To accommodate smoother transitions, the MVs were tuned with GEKKO parameters to discourage volatility. These proved difficult to control because attempts to constrain them with DCOST or DMAX resulted in the controller becoming unresponsive. Many ranges of DCOST or DMAX values were attempted and either caused no effect, or caused the controller to stop achieving the setpoint altogether. However the use of CV parameter tuning proved effective for this system. The one CV, melt index, was assigned CV parameters to encourage the controller to achieve multiple setpoints while lowering transition times and spikes in MVs. These parameters are: TAU = 0.3, TR_INIT = 2, TR_OPEN = 2. Using these settings, the controller was able to approach the setpoint more aggressively without increasing the spikes in the inlet flow rates. In addition to these constraints, a COST value was applied to the production rate. The value of the cost was set proportional to the square of the difference between the setpoint and the current MI value. This lowered the polymer production rate while the system was not meeting MI requirements. Figure 4 shows the controller with an aggressive TAU = 0.3. Figure 5 shows the controller with TAU = 0.5.

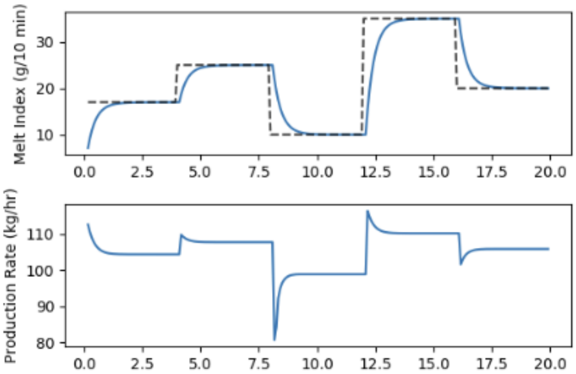

Figure 4: MPC with tuning

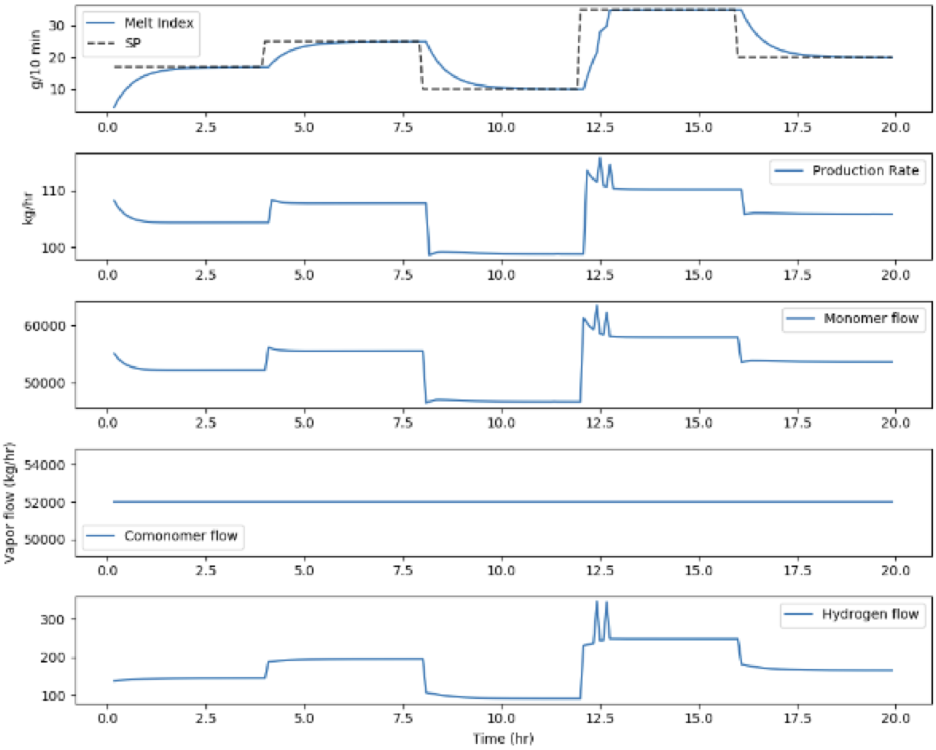

Figure 5: MPC without tuning

5 Discussion and Future Work

The model produced is a good beginning for modeling a PO reactor. More would need to be added for it to be consistent with actual data. The next step would be to include a catalyst feed and a reflux for unreacted gas. Adding these will make the model applicable to most styles of PO reactors. Next, energy balances and thermodynamics would need to be added to the model. This would produce greater variation in the reaction rates and more realistic results. Some approximations will be necessary to prevent the model from becoming too complex. The equations would come from energies of reaction for the system, rates of heat exchange with a cooling jacket, and specific heat estimations for all of the contents of the reactor.

Once a working model with thermodynamics is achieved, the next step would be to include an inert such as pentane in our reactor feed to help regulate heat within the reactor. Pentane can make the process more stable by vaporizing and absorbing heat given off by polymerization. Some step tests would be needed to approximate the response of the pentane in the reactor because of the discontinuous nature of the vaporization of pentane. The objective would be to optimize the amount of pentane fed to the reactor and the cooling needed to condense it once it has left the reactor, along with minimizing transition-state waste product.

6 Conclusion

The objective of this project was to create a model of a PO reactor that would model the condensed-phase heat exchanger with a pentane inert and optimize the transition states between MI grades of polymer. The project began with a model that could be amended and optimized to transition between polymer grades. The model never was able to simulate, so another model type was chosen. The next model type attempted was a PO model using a method of moments to determine reaction rates. This was based heavily on Reza-Abbassi's model and his paper. Dr Hedengren advised against using a method of moments and suggested the use of a simple concentration-based system and provided a model to work from. This model is what was used for the simulation and control. Solutions were found for the optimization of the change in the polymer grade in the PO reactor.

For the future, more equations and relations would need to be added to a model to achieve condensed phase heat exchanger optimization. It will need energy balances, heat transfer equations, catalyst input, inert condensation, and reflux of unreacted gas. To achieve the initial goal, step tests would be essential to understand the response of the inert in the reactor and its heat absorption. Once a correlation is found, a controller would be able to accurately optimize the production rates.

7 References

[1]Abbasi et al. "Dynamic modeling and Molecular Weight Distribution of ethylene copolymerization in an industrial gas-phase Fluidized-Bed Reactor" Advanced Powder Technology. Volume 27, Issue 4, 2016, Pages 1526-1538

[2]McAuley et al. "Modelling, Estimation and Control of Product Properties in a Gas Phase Polyethylene Reactor" (PhD Dissertation) McMaster University. 1991