Modeling of High-Pressure Processes for Homo-, Co-, and Terpolymerization

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Introduction
This research explores the modeling and simulation of the high-pressure processes of ethene homopolymerization, ethene-propylene copolymerization, and ethene-vinyl acetate-propylene terpolymerization, all based upon empirical data from an autoclave mini-plant. Simulation aided product design is frequently applied to describe the high-pressure process of ethene polymerization and its comonomers. These simulations allow for the prediction of large scale changes of polymer properties with a chosen set of initial process conditions.

Ethene Polymerization Basics
The polymerization of ethene follows the below reactions. The modeling however only considers all of the reactions except the propagation of terminal double bonds (DB).

Simulation Methods
This research uses a three-step modeling technique, which includes deterministic modeling of kinetics, stochastic modeling of microstructure, and rheology modeling of flow behavior. Among other properties, the deterministic modeling outputs reaction frequencies. The stochastic models calculate probabilities of reaction paths from these reaction frequencies, and output the topology of individual macromolecules. From this topology a rheology model can then calculate properties such as relaxation, viscosity, and processability. This work only explores deterministic and stochastic modeling.

Kinetics Simulation with Predici
Predici 7 (Polyreaction Distribution by Countable System Integration) is used to model the homopolymerization of ethene, the copolymerization of ethene and propylene, and the terpolymerization of ethene, vinyl acetate, and propylene (EVAP).

Stochastic Simulation with Monte Carlo
A hybrid Monte Carlo model is used to simulate the microstructure of the homopolymerization of ethene. The Monte Carlo transforms the reaction frequencies outputted by the Predici model. While the simulation iterates over time steps, incrementing a molecule’s residence position. For every time step, the found probabilities are compared against random numbers to simulate these reactions.

Terpolymerization Method
This research attempts to create a model to simulate the terpolymerization of EVAP. To achieve this, a model of ethene-vinyl acetate (EVA) copolymerization was combined with another model of ethene-propylene (EP).

Results
The numerical homopolymerization of ethene simulation is broken into five experiments with heptane as a chain transfer agent (CTA) and three without CTA. The above figures are one experiment out of these two sets, with NoCTA01 the polymerization with no CTA and Heptane 02-02 with heptane CTA. The simulation Mn distribution fits nicely to the experimental distribution, where the peak width is in the same shape and the peak maximum in the correct position. The simulation with heptane CTA doesn’t fit exactly in higher chain lengths because of fouling effect from an older version of the mini-plant. These are not seen in the experimental without CTA because the mini-plant was updated to fix this issue.

The stochastic ethene homopolymerization simulation achieves good results with a low error when comparing Predict model found Mn with the experimental at one million molecules and with increasing molecules the deviation becomes smaller. However this deviation is still too high to move onto a rheological simulation. This deviation stems from the Monte Carlo model which handles backbiting differently than Predict.

Conclusions
Progress toward evaluating the deviation of an industry partner’s correlation between chain length and melt flow rate was made with the successful development of numerical and stochastic simulations of the high-pressure process of ethene homopolymerization. Progress toward developing a copolymerization and terpolymerization model of ethene-propylene and ethene-vinyl acetate-propylene was made and challenged previous assumptions. In the future, these models will be used to continue evaluating high-pressure polymerization processes.

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Motivation
The working group Busch utilizes a relationship between the melt flow rate (MFR) and the average change length of a polymer (Mn) given by an industry partner based upon empirical data. MFR is the mass flow rate of a melted thermoplastic under a desired pressure in 10 minutes.

When applied to the high-pressure polymerization of ethene in our mini-plant, the relation deviates. This deviation can be explored through the use of a rheological simulation of the polymerization process.