Detailed Modeling of LDPE Autoclave Reactors

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Highlights
- Detailed model combining rigorous thermodynamics, full molecular weight distribution modeling, and accurate flow patterns derived from CFD simulation.
- Validation against commercial reactor operating data achieved by adjusting a small set of kinetic parameters.
- The validated model has been applied to increase production in existing commercial reactors while preserving desired product properties.

1. Introduction
Developing new polymer grades typically presents a number of challenges – for example, determining the necessary operating conditions for producing desired polymer molecular weight distributions (MWD) in reactor systems with imperfect mixing and complex kinetics. This presentation describes how an integral modeling approach that combines the advantages of SAFT physical property predictions, detailed kinetic modeling, and characterization of flow and mixing patterns using Computational Fluid Dynamics (CFD) captures the effect of changes in operating conditions on the shape of MWDs. This type of modeling work helps in reducing development time for new polymer grades, and in evaluating new reactor designs. It has also been applied in the determination of operating conditions that preserve polymer properties when changing reactor throughput.

2. Methods
Detailed models of industrial Low-density polyethylene (LDPE) autoclave reactors have been built by integrating several advanced modeling concepts:

(a) An advanced thermodynamic model based on the Statistical Association Fluid Theory (SAFT) γ-Mie Equation of State, which represents molecules as chains of distinct functional groups [1-3]. Each group is characterized by its own size. Self-interactions of a specific functional group (i.e. interactions with identical functional groups) and interactions with other groups are characterized by their own Mie-potentials. This approach is ideally suitable for the modeling of polymers.

(b) Kinetic modeling in perfectly stirred reactor zones that considers elementary reaction steps in chemically initiated free radical polymerization [4,5] and solves for the evolution of the full molecular weight distribution (MWD) using the fixed pivot technique (PFT) [6].

(c) A multi-zonal approach [7] to represent the complex flow pattern in industrial-size autoclave reactors. The reactor is represented as a network of perfectly stirred reactors, and the flows among the various reactors are calculated by processing the results of a “cold-flow” Computational Fluid Dynamics (CFD) simulation of the reactor.

The integrated reactor model is built on Process Systems Enterprise’s (PSE) gPROMS® advanced process modeling platform using PSE’s gSAFT thermodynamic engine and PSE’s Hybrid Multizonal gPROMS-CFD tool for automatic processing of results of CFD simulations performed with ANSYS Fluent®.
3. Results and discussion

The integrated modeling approach has several advantages that enable more accurate modeling of LDPE autoclave reactors:

- The use of a rigorous thermodynamics allows us to incorporate the effect of temperature and pressure on the heat of reaction, improving temperature predictions. The approach also allows accurate prediction of the on-set of two-phase behavior of reacting mixtures, accounting for polydispersity and branching (Figure 1).

- Detailed kinetic modeling allows prediction of the full molecular weight distribution, including the high molecular weight shoulder seen in many LDPE grades.

- Multizonal modeling with a sufficiently large number of zones (200-300) allows the model to respond to changes in design details, such as shaft, paddle, and baffle geometry, and positioning and orientation of injection ports.

- Implementation on the gPROMS platform allows us to take advantage of standard features such as (i) parameter estimation to adjust kinetic parameters to match plant data, and (ii) optimization to find operational set points that achieve desired product properties, such as Melt Index and resin density.

References


Keywords

Autoclave reactors; Low-density polyethylene; Molecular weight distribution; Fixed pivot technique